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THE

ELEMENTS OF HEAT

AND OF

NON-METALLIC CHEMISTRY.

ESPECIALLY DESIGNED FOR CANDIDATES FOR THE
MATRICULATION PASS EXAMINATION OF
THE UNIVERSITY OF LONDON.

BY

FREDERICK GUTHRIE,
B.A. (LOND.), PH.D., F.R.S.E., F.C.S.,
LATE PROFESSOR OF CHEMISTRY AND PHYSICS, ROYAL COLLEGE, MAURITIUS.

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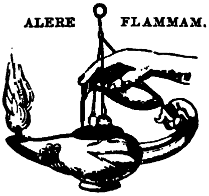


PREFACE.

THIS little treatise is intended for the use of Candidates for the Matriculation Pass Examination of the University of London. It is believed to contain all (and but little more than all) that is required for the chemical branch of that examination.

On page ix will be found a list of the subjects in this branch, a knowledge of which is demanded by the University. Attached to each is given the number of page and paragraph where the subject is discussed. It will be seen that the order of the subjects required for the examination has been adhered to as strictly as possible.

There is in each Chapter about sufficient material for a lesson. Those to whom the subject is entirely new and who have not the advantage of receiving oral instruction, should not attempt to understand everything on the first reading. They should read the book carefully, but rapidly, once or twice, so as to gain a general idea of the nature of the subject. After being laid aside for a time, the book should be taken up again and studied so as not to leave a single point in obscurity.

The considerable changes which have recently been introduced into the views regarding the composition of many bodies, have received careful consideration. The combining weights or equivalents of the elements here given are those almost universally employed in this country. The chemical names given to the various compounds are those which will be found to be at present the most useful to the generality of students. All controversial matter has been avoided.

On page 203 will be found a number of questions, many of which have been given at the Matriculation Pass Examination. Attached to each question is a reference to the paragraph where the subject is considered. The student should be able to answer all these questions.

Although the book has the special aim mentioned, it is hoped that it may serve as a sound introduction to further studies.

London,
September 1868.

CONTENTS.

PART I.

HEAT.

CHAPTER I.

PAGE
General Notions 1

CHAPTER II.

Sources of Heat 3

CHAPTER III.

Expansion 7

CHAPTER IV.

Thermometers 22

CHAPTER V.

Relation between the Thermometric Scales in common use 28

CHAPTER VI.

Difference between Temperature and Quantity of Heat 32

CHAPTER VII.

PAGE
Specific Heat 36

CHAPTER VIII.

Calorimeters 38

CHAPTER IX.

Latent Heat 41

CHAPTER X.

Liquefaction 45

CHAPTER XI.

Evaporation and Ebullition 46

CHAPTER XII.

Ebullition 54

CHAPTER XIII.

Conduction of Heat 58

CHAPTER XIV.

Convection of Heat 63

CHAPTER XV.

Radiation of Heat 64

PART II.

CHEMISTRY OF THE MORE IMPORTANT NON-METALLIC ELEMENTS.

CHAPTER I.

PAGE
General Notions 71

CHAPTER II.

Atomic hypothesis. Combination by Weight and by Volume. Equivalents 78

CHAPTER III.

Symbols and Nomenclature 88

CHAPTER IV.

Acids, Bases, and Salts 93

CHAPTER V.

Oxygen 98

APPENDIX TO CHAPTER V.

Numerical Calculation &c. 103

CHAPTER VI.

Hydrogen and its compounds with the preceding element 105

CHAPTER VII.

Nitrogen and its compounds with the preceding elements 114

CHAPTER VIII.

PAGE
CARBON AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS 128

CHAPTER IX.

CHLORINE AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS 140

CHAPTER X.

BROMINE AND IODINE, AND THEIR COMPOUNDS WITH THE PRECEDING ELEMENTS 147

CHAPTER XI.

FLUORINE AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS 155

CHAPTER XII.

SULPHUR AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS 157

CHAPTER XIII.

PHOSPHORUS AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS 169

CHAPTER XIV.

SILICON OR SILICIUM AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS 177

CHAPTER XV.

COMBUSTION AND FLAME 182

CHAPTER XVI.

THE ATMOSPHERE 194

CHAPTER XVII.

NATURAL WATERS 199

INDEX

showing the subjects required for the " Chemical " branch of the Matriculation Examination, and the page and paragraph where they are discussed.

PART I.

	Pages	§§	Chap.
Heat (general notions)	1–3	1–7	I.
Sources of heat	3–6	8–16	II.
Expansion	7–22	17–43	III.
Thermometers	22–27	44–54	IV.
Relations between different thermometric scales in common use	28–30	55–56	V.
Difference between temperature and quantity of heat	32–35	59–68	VI.
Specific heat	36–37	69–77	VII.
Latent heat	41–45	85–96	IX.
Calorimeters	38–41	78–84	VIII.
Liquefaction	45–46	97–102	X.
Ebullition	54–57	129–139	XII.
Evaporation	46–54	103–128	XI.
Conduction	58–62	141–162	XIII.
Convection	63–64	163–168	XIV.
Radiation	64–70	169–185	XV.

PART II.

Chemistry of the non-metallic elements (general notions)	71–78	1–23	I.
Oxygen	98–103	75–85	V.
Hydrogen	105–109	87–95	VI.
Carbon	128–130	146–150	VIII.
Nitrogen	114–115	110–113	VII.
Chlorine	140–143	178–186	IX.
Bromine	147–148	199–200	X.
Iodine	150–151	205–208	X.
Fluorine	155	215	XI.
Sulphur	157–159	221–223	XII.

	Pages	§§	Chap.
Phosphorus	169–171	253–257	XIII.
Silicon	177–179	277–281	XIV.
Combining proportions by weight and by volume	78–87	24–41	II.
General nature of acids, bases, and salts	93–98	57–74	IV.
Symbols and nomenclature	88–93	42–56	III.
The atmosphere—its constitution; effects of animal and vegetable life upon its composition	194–198	327–339	XVI.
Combustion: structure and properties of flame	182–191	295–316	XV.
Nature and composition of ordinary fuel	191–194	317–326	XV.
Water	109–113	96–108	VI.
Chemical peculiarities of natural waters, such as rain-, river-, spring-, and sea-water	199–202	340–349	XVII.
Carbonic acid	130–132	152–159	VIII.
Oxides and acids of nitrogen	115–122	114–132	VII.
Ammonia	123–127	133–144	VII.
Olefiant gas	134–136	164–168	VIII.
Marsh-gas	136–138	169–172	VIII.
Sulphurous and sulphuric acids	159–164	224–235	XII.
Sulphuretted hydrogen	164–166	236–241	XII.
Hydrochloric acid	144–146	191–195	IX.
Phosphoric acid	171–172	258–261	XIII.
Phosphoretted hydrogen	173–175	265–266	XIII.
Silica	179–180	282–286	XIV.

ELEMENTS

OF

HEAT AND NON-METALLIC CHEMISTRY.

PART I.

HEAT.

CHAPTER I.

General Notions.

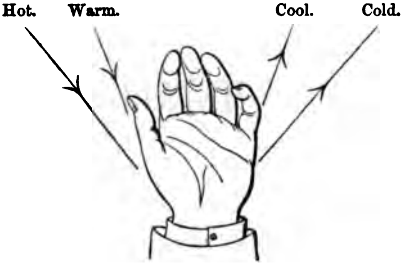
§ 1. Heat is that physical force which causes, or tends to cause, change in the temperature of bodies.

§ 2. All known matter contains more or less heat. It receives heat when it becomes warmer; it gives heat out when it becomes colder, in all cases unless change of physical state takes place. There is therefore no such thing as cold, except as the comparative absence of heat.

§ 3. When two bodies of different temperature are in contact with one another, heat always passes from the warmer to the colder body, until the temperature of the two becomes the same.

§ 4. A body is, in familiar language, called hot or warm according as it gives more or less heat to the hand, or other part of the body in contact with it. It is said to be cool or cold according as the hand gives less or more heat to it. Thus, in fig. 1, the direction of the arrows may represent the direction in which the

Fig. 1.



heat moves (to or from the hand), and the length of the arrows may represent the relative quantity of heat which passes. Hence all bodies feel hot or warm whose temperature is higher than that of the blood; they feel cool or cold when their temperature is lower than that of the blood.

§ 5. The sense of heat is conveyed to the brain by the same nerves as convey the sense of touch; so that most parts of the surface of the body, except the hair and nails, are sensitive to change of temperature—that is, to gain or loss of heat. If only a small part of the body be subjected to violent change of temperature, the sensation produced may be the same, whether that change be a gain or loss of heat.

§ 6. The action of heat on inanimate matter is recognized through the eye chiefly:—(*a*) by the way in which bodies are affected by it, in regard to size, shape, and physical state (change of solids, liquids, and gases into one another); (*b*) by the changes it causes in the luminosity, colour, and other optical properties of the substances upon which it acts; (*c*) by its influence upon magnetism and electricity; (*d*) by its effect upon the chemical constitution of bodies. Of these visible effects of heat we have only to consider (*a*) and (*d*); the latter can be discussed only after gaining some idea of chemical change (Part II.).

§ 7. Little is known concerning the nature of heat. It is, with great reason, supposed to consist of vibrations in some unknown medium or æther, which is imagined to pervade all space and all matter. According to this supposition, one body is hotter than another when the vibrations of the æther of the first are more violent than those of that of the second. One body gives heat to another by communicating its ætherial vibrations to the æther of the second, and so on*. It is, however, simpler, and will be amply sufficient for our purpose to conceive heat as something without appreciable weight or mass, and whose loss or gain by bodies produces certain sensational, physical, and chemical effects.

CHAPTER II.

SOURCES OF HEAT.

§ 8. Strictly speaking, all known bodies are possible sources of heat, because they all contain heat, and will give up part of that heat to bodies of a lower temperature. But certain bodies, and bodies under certain conditions, are so much hotter than neighbouring bodies and give heat to the latter so habitually, that they are looked upon as special sources of heat.

§ 9. *The Sun* is the chief source whence the earth receives heat. It is calculated that the earth receives every year from the sun enough heat to melt a coating of ice enclosing the earth of a thickness of 34 yards. Probably also the fixed stars give a little heat to the earth; but neither their heat, nor that, if any, given to the earth by the moon, has been determined, being too small for measurement.

§ 10. *The earth itself* is, in all probability, very much hotter towards the interior than it is on the surface. That such is the case is rendered probable by the occasional breaking forth of melted rock or lava from active volcanoes. The existence of natural hot-springs points to the same conclusion. Further, on descending deep mines, the temperature is found to increase continually with the depth; and the water from very deep wells is found to be hotter than that from shallower wells. On the whole, the earth has not sensibly decreased or increased in temperature within human records.

---

* What is usually called "the dynamical theory of heat," supposes that the particles of the matter itself are in vibration. This hypothesis, alone, appears incompetent to account for the transmission of heat through space void of ponderable matter, as in the case of solar heat.

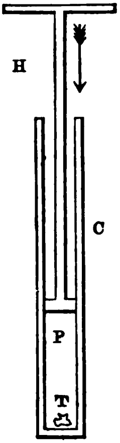
11. *Friction.*—When the surfaces of any two substances whatever move over one another in contact, heat is invariably given out by both. The quantity of heat produced by friction varies with the labour expended in effecting motion—that is, with the amount of friction. Rough solids having greater friction than smooth ones, greater heat is produced by their motion upon one another, other things being equal. For the same reason, less heat is produced by the friction of liquids than by that of solids, and still less by the friction of gases. Examples of heat, caused by the friction of solids, are found in the lighting of a match, the warmth produced by rubbing the hands, the scorching and ignition of a piece of hard dry wood when it is rubbed violently on a soft board, the burning of the edge of a boat by the rapid motion over it of a whale-rope. The heat generated by the friction of iron disks has been employed for heating houses. A rod of iron may be made hot enough to ignite wood by quick and heavy hammering; this effect is chiefly due to the friction of the parts of the iron on one another. Ice may be melted by rubbing two pieces together.

That the friction of liquids produces heat, is seen from the fact that still water freezes more readily than that which is agitated. The temperature of the water in a bottle is sensibly raised on shaking it violently. The warmth of animals is partly caused by the friction of the blood in their arteries and veins.

The wind gives rise to heat by its friction upon itself and upon the solids and liquids it meets with. The temperature of a dry solid may be sensibly raised by whirling it rapidly through the air. Aërolites become red-hot on entering and tearing through the atmosphere.

§ 12. *Change of density by pressure.*—Whenever a fixed quantity of gas undergoes diminution of volume by pressure, heat is evolved. Thus, if C (fig. 2) be a cylinder containing a fragment (T) of German tinder, and if a close-fitting piston (P) be inserted at the top and forcibly and rapidly pressed down towards T by means of the handle and rod H, the original volume of air in the cylinder will be compressed into the space between the bottom of the piston and the bottom of the cylinder. As the air becomes thus more and more compressed, it gets hotter and hotter, until at last it may set fire to the tinder.

Fig. 2.



The barrel of an air-gun becomes hot as the air is pumped into it.

It is probable that solids and liquids also give out heat when mechanically compressed. Their change of volume is, however, so slight, under the greatest attainable pressures, that the heat, if any, liberated is inappreciable.

§ 13. *Change of physical state.*—When a vapour is condensed into a liquid by pressure or other means, heat is given off. Thus steam, at the temperature of boiling water, if forcibly compressed, condenses into water, having a higher temperature. Gases, when they dissolve in water or other liquids, thereby themselves becoming liquid, give out heat.

Liquids, when they become solid, give out heat. With some precautions, many salts may be dissolved in water in such quantities that, on the slightest agitation, the salt crystallizes out; in doing so it becomes warm. Water itself, if kept quite still, may be cooled below the temperature at which it ordinarily freezes; when disturbed, part of it becomes ice and, in doing so, rises in temperature. This source of heat will be further considered in §§ 96–137, under liquefaction, ebullition, evaporation.

The following diagram shows the relation of heat to the three forms of matter—solid, liquid, and gaseous,—the direction of the arrows denoting the kind of change of physical state.

Fig. 3.

Heat given out.
Gas → Liquid → Solid.
(Example.) Steam Water Ice.

§ 14. *Chemical change.*—When two different kinds of matter are brought into contact, they often interpenetrate and unite in a peculiarly intimate manner, giving rise to a product different from both. This action is called chemical union; its consideration forms a main portion of Part II. Chemical union is always attended by the liberation of heat. The solid quicklime, in contact with the liquid water, is converted into slaked lime, becoming hot. When heated together, a part of the air (a gas) unites with carbon (a solid), giving rise to a heavy irrespirable gas, and producing fire. The same part of the air may unite with fat, wax, wood, paper, spirits of wine, &c., giving rise to the same gas, together with vapour of water, and producing flame. The heat of fermentation, putrefaction, and decay is also caused by chemical change.

Chemical change, of which burning or combustion is the most common instance, furnishes most of the heat produced artificially for the purposes of life.

§ 15. *Electrical discharge,* both of frictional or high-tension and of voltaic or low-tension electricity, gives rise to heat. Instances of the former are seen in the burning or fusion of bodies by lightning, and the burning or volatilization of thin wire by the artificial spark. Instances of the latter occur when a voltaic circuit is completed or broken; when it has to traverse a substance of conducting-power insufficient to allow it to pass freely (a narrow wire), or when a strong current has to leap over a short interval (the heat of the electric light).

§ 16. *Living beings* are generally of a higher temperature than the surrounding media. This is sometimes attributed to what is called *Vital heat.* Such heat is probably mainly due to the chemical changes and electrical discharges taking place in the tissues, and to the friction of the juices.

CHAPTER III.

EXPANSION.

§ 17. Almost all bodies, whatever be their temperature, and whether they be solids, liquids, or gases, expand or increase in volume when they increase in temperature. This is supposed to be due to the heat, on entering the body, separating its particles further from one another than they were when the body was cooler.

§ 18. *Expansion of gases by heat.*—All gases, at all temperatures, expand equally for equal increases of temperature*. Thus, if cubic feet of all known gases, at the temperature of melting ice, be heated to the temperature of boiling water, they all increase equally in bulk, each one becoming $1+\frac{100}{273}$ cubic foot—that is, 1·366 cubic foot. On cooling them to the original temperature, they all shrink equally, resuming their original volume of 1 cubic foot.

Further, if they all be heated to any the same intermediate temperature, they will all have the same size, intermediate between 1 and 1·366 cubic foot.

Again, if they all be heated to a temperature exactly halfway between those of melting ice and boiling water, they will all have exactly the same volume ($1+\frac{\cdot 366}{2}=1\cdot 183$ cubic foot). And if they be made as much hotter than boiling water as boiling water is hotter than melting ice, they will all have the volume $1+2\times\cdot 366=1\cdot 732$ cubic foot.

In general terms, if we suppose the range of temperature between melting ice and boiling water to be divided into 100 equal parts or "degrees," the increase of volume which a given volume of the gas undergoes (on being heated through one of those degrees) is $\frac{1}{100}$ of its increase when heated through 100 of them; and its increase on being heated through n of such degrees is $\frac{n}{100}$ of its increase when heated through 100 of them; that is, $\frac{n}{100}$ of ·366, or $n \times \cdot 00366$. The entire volume of the heated gas is therefore its original volume at the lower temperature, together with this increase; or if V_1 be the original volume at the lower temperature, and V_2 be the volume at a temperature t degrees higher, then

---

* This law is not of absolute truth under all circumstances, but quite sufficiently so for all ordinary purposes.

$$\begin{aligned} V_2 &= V_1 + V_1 \times t \times \cdot 00366 \\ &= V_1(1 + t \times \cdot 00366), \end{aligned}$$

and

$$V_1 = \frac{V_2}{1 + t \times \cdot 00366}.$$

Example 1.—20 cubic centimetres of air at 12 degrees are heated to 26 degrees; required the volume of the warmer air.

Here $V_1 = 20$ cub. centims., $t = 26 - 12 = 14$;

$$\begin{aligned} \therefore\ V_2 &= 20 \text{ cub. centims.} + 20 \times 14 \times \cdot 00366 \\ &= 21 \cdot 0248 \text{ cub. centims.} \end{aligned}$$

Example 2.—48 cubic centimetres of hydrogen at 51 degrees are cooled to 17 degrees; required the volume of the cooler gas.

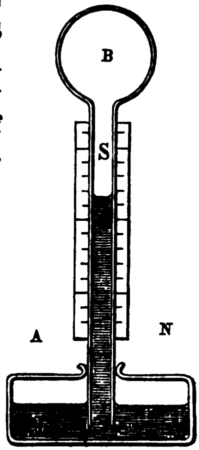
Here $V_2 = 48$ cub. centims., $t = 51 - 17 = 34$;

$$\begin{aligned} \therefore\ V_1 &= \frac{48}{1 + 34 \times \cdot 00366} \\ &= 42 \cdot 69 \text{ cub. centims.} \end{aligned}$$

§ 19. It is to be remembered that if the quantity or weight of a substance remains the same, its density varies inversely as its volume. We know also, by Boyle and Mariotte's law, that the volume of a gas varies inversely as the pressure to which it is exposed. (See Pneumatics.) We are now, therefore, able to determine the volume of a gas at any given temperature and pressure, if we know its volume at any other temperature and pressure. Such reductions are very important in studying the combinations of gases by volume (Part II.), and in gas-analysis.

§ 20. The expansion of a gas by heat may be shown by inverting (fig. 4) a bulb, B, attached to the tube S, open at the bottom into a vessel, A, partly filled with a coloured liquid, L, in such a manner that the open end of S dips into the liquid L and S passes loosely through N, the neck of A. On warming B, the air in it expands, and a few bubbles are expelled through the open end of S. On allowing B to cool, the air in it shrinks to its original density; but some having escaped, the volume of the remainder is less than before. The pressure of the atmosphere on the surface of L forces the coloured liquid to rise in S to a certain height, depending upon the quantity of air expelled. Any source of heat, such as the warm hand applied to B, expands the air in it and forces the liquid down the stem S. The greater the heat applied to B the lower the liquid sinks in S.

Fig. 4.



§ 21. The expansion of gases by heat is also seen on holding a shrivelled apple, or a bladder partly filled with air, and closed at the neck, before the fire: the air within expands and distends the skin.

Fig. 5.

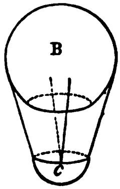
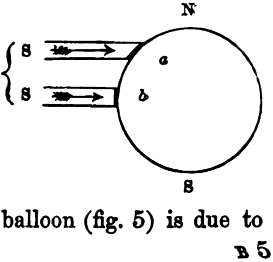


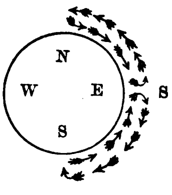
Fig. 6.



§ 22. The ascent of a fire-balloon (fig. 5) is due to the same cause. A balloon, B, having a wide mouth, carries a cup, C, containing some spirits of wine. On setting fire to the spirits of wine the resultant gases ascend, being hot and therefore light, into the balloon, which therefore becomes filled with a mixture of gases lighter than air. The balloon rises.

§ 23. The effect of heat in altering the volume, and thereby the density of a gas, is seen on a very large scale in nature, in the formation of the " trade-winds." Imagine (fig. 6) two equal quantities of heat to fall in a parallel direction on the earth from the sun. That which falls upon the earth towards the north pole strikes the surface obliquely, and is distributed over the surface *b*. The same quantity falling at the equator is spread over the surface *a*. It is clear that the surface *b* is greater than the surface *a*, and that therefore the intensity of the heat at *a* is greater than the intensity at *b*. The earth at the equator consequently heats the air in contact with it more than does the earth at *b*. The air at the equator expands more, becomes lighter, and rises. To supply its place, the cooler air from the polar regions rushes along the surface of the earth towards the equator while the air which has been warmed and raised at the equator, travels towards the polar regions. The same takes place in both hemispheres, so that (fig. 7) the upper and warmer parts of the air move from the equator towards the poles, while the lower and cooler move from the poles towards the equator. The latter are the trade-winds. The daily rotation of the earth and all upon it towards the east, makes it appear as though these lower winds blew from the north-easterly and south-easterly quarters in the northern and southern hemispheres respectively.

Fig. 7.



§ 24. Hot air ascends a chimney. The art of ventilation mainly consists of allowing passages for the escape of hot air near the top of a room, and for the entrance of cool air near the bottom. The flame of a candle held to the crack of a door of a hot room, will be blown inwards towards the bottom of the crack, outwards towards the top.

§ 25. *Expansion of liquids by heat.*—All liquids at all temperatures expand by increase of temperature, with the very important exception of water near its freezing-point. This exceptional case will be considered immediately. All other liquids when they increase in temperature, increase also in bulk, and consequently become less dense. On cooling to their original temperatures, they also, like gases, resume their original volumes.

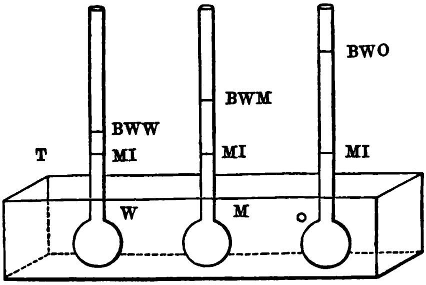
§ 26. But different liquids, having originally the same temperature, expand unequally for the same increase of temperature; and the same liquid almost invariably expands to a slightly different amount on being heated the same amount, when its original temperature is different.

Thus, if equal volumes, say, cubic feet, of oil, mercury, and water, all at the temperature of melting ice, be all heated to the temperature of boiling water, the oil will expand most, the water least, and the mercury to an intermediate amount.

§ 27. Again, if a cubic foot of oil be heated from any temperature to a higher one, it expands a certain quantity; if a cubic foot of the hot oil be then heated, so that its last temperature is as much above its second as its second temperature was above its first, its second increase of volume will be greater than its first. It may be taken as a general law that the hotter a liquid is, the more the same volume of it expands for the same increase of temperature.

§ 28. The differences between the expansions of different liquids

Fig. 8.



of the same temperature, for the same increase of temperature, may be shown in the following manner. Let exactly the same volumes, at the temperature of melting ice, of oil, mercury, and water be respectively placed in the three stemmed bulbs O, M, W, of exactly the same capacity, so that, when they are all plunged into melting ice in the trough T, the liquids in all may stand at the same height, M I. If, now, the ice in T be melted to water, and the water be further heated until it boils, the level of the oil in its stem will be B W O, that of the mercury B W M, while that of the water will be lowest, and stand at B W W. The volumes contained in the several parts of the stems between M I and B W O, B W M, B W W respectively, are the increases of volume which the liquids undergo on being heated through this particular range of temperature.

§ 29. More accurate results are obtained in the following manner. A little bottle (fig. 9), provided with a stopper (which is bored through by a fine hole, and which is enlarged above into a sort of cup), is filled up to the mark *a*, while surrounded by melting ice, with the liquid under examination. Then it is taken out and weighed. If the weight of the empty bottle be w_1, and its weight, when full of liquid, be w_2, then $w_2 - w_1$ is the weight of its liquid contents. It is then plunged into boiling water, whereupon the liquid rises into the cup; it is wiped off so as to stand again at *a*, its original height. The bottle is withdrawn, wiped, allowed to cool, and again weighed. Let its weight be w_3. Then $w_3 - w_1$ is the weight of the hot liquid; and $w_2 - w_3$ is the weight of the liquid which has been removed; that is, the weight of the increase of the volume of the liquid.

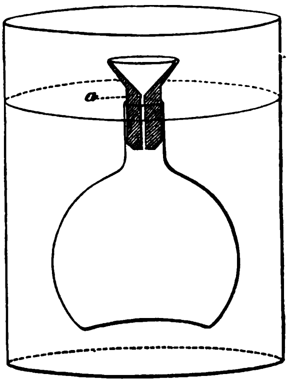


Fig. 9.

Since, finally, the weights of the same liquid are proportional to their volumes, we find, putting V_1 for the volume at the temperature of melting ice, and V_2 for the volume at the temperature of boiling water,—

$$\frac{\text{increase of volume}}{\text{original volume}}=\frac{V_2-V_1}{V_1}=\frac{w_2-w_3}{w_2-w_1};$$

$$\therefore V_2=V_1+V_1\frac{w_2-w_3}{w_2-w_1}.$$

Example.

The bottle empty weighs	$3{\cdot}2495=w$
„ „ full of cold oil weighs	$12{\cdot}4320=w_2$
„ „ with the amount of cold oil which filled it when hot..	$11{\cdot}9630=w_3$.

Then

$$\frac{\text{the increase of volume}}{\text{the original volume}}=\frac{w_2-w_3}{w_2-w_1}=\frac{{\cdot}4690}{9{\cdot}1825};$$

$$\therefore \text{the increase of volume}=V_1\times\frac{{\cdot}4690}{9{\cdot}1825};$$

$\therefore$ the increased volume V_2

$$=\text{original volume}+\text{increase of volume},$$

$$\text{or } V_2=V_1+V_1\frac{{\cdot}4690}{9{\cdot}1825};$$

so that, for instance, three cubic feet would become

$$3+3\times\frac{{\cdot}4690}{9{\cdot}1825}$$

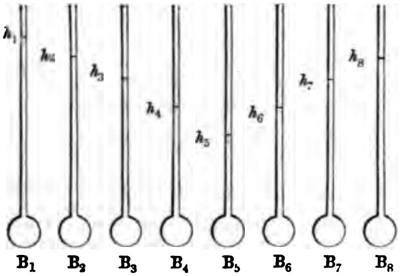
$$=3{\cdot}153 \text{ cubic feet.}$$

§ 30. The following list shows the differences of the total expansion of a few liquids, when heated through a tenth of the range from the melting-point of ice to the boiling-point of water.

100 volumes become, of water	100·02
„ „ mercury	100·18
„ „ oil of bitter almonds..	100·93
„ „ alcohol	101·05
„ „ wood-spirit	101·15
„ „ ether..............	101·52

§ 31. Water, as before mentioned, shows a remarkable and almost singular irregularity in its expansion by heat. Imagine there to be a bulb, B, with a stem, as before, filled up to h with ice-cold water. On allowing the water to get warm, the level h_1 is found at first to sink to h_2, showing that the increase of temperature, instead of expanding, contracts the water, which therefore increases in density. On a further accession of heat, the water further shrinks to h_3, then to h_4, and finally to h_5. If it be still further warmed, it begins to expand, and reaches h_6, h_7, h_8 in succession; and henceforth and up to the temperature at which it boils, it obeys the same law as other liquids, namely, continual expansion for continual increase of temperature.

Fig. 10.



Inversely, if the water be originally hot and then be gradually cooled, it shrinks on cooling, its level becoming successively h_7, h_6, h_5; beyond this point, as it loses heat, it again expands, reaching the levels h_4, h_3, h_2, h_1; having attained which last level, it begins to freeze.

The temperature at which any quantity of water has its least volume, is called its "temperature of maximum density." It is very little higher than the temperature at which ice melts or water freezes. If, as before, we imagine the whole range of temperature between melting ice and boiling water to be divided into 100 equal parts or degrees, then water has its maximum density when its temperature is four of those degrees above the melting-point of ice. We shall understand this after the description of thermometers as being +4 degrees on the Centigrade scale (written 4° C.).

The same fact is shown on taking a vessel of warm water into a very cold room. The water at the surface, in contact with the cold air, is first cooled, and having become reduced to +4° C. (that is, to the temperature of greatest density) it sinks to the bottom of the vessel. This goes on until the whole of the water has attained the same temperature and state of maximum density. The water at the surface, however, still continues to lose heat; but it no longer shrinks on doing so, because all further loss of heat tends to make it lighter. At last a crust of ice is formed on the top, which gradually thickens. It is, in fact, owing to the maximum density of water being at a temperature higher than its freezing-point that ice always forms only on the surface of still water cooled from above. It is of great importance that such should be the case, and that freezing water itself at the moment of solidification should undergo a further increase of bulk, so that ice is lighter even than ice-cold water. For were the reverse the case, it would sink as soon as formed and accumulate during the winter at the bottoms of rivers, lakes, and seas. There, protected by the water above, it would resist the action of the sun and greatly modify the climates of temperate regions. Still water which has commenced to freeze, when examined as to its temperature, presents the following appearance (fig. 11).

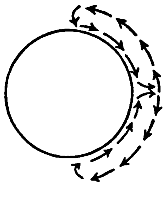
Fig. 11.

Cold ice.....................	(−1° C.)
Ice..........................	(0° C.)
Water	(0° C.)
,, ...	(1° C.)
,, ...	(2° C.)
,, ...	(3° C.)
,, ...	(4° C.)

§ 32. In taking the specific gravity of solid substances by immersing them so as to float, or weighing them in water, and of liquids, by weighing equal volumes of them (see Natural Philosophy), regard must be had to the change of density caused by change of temperature, and either the temperature at which the experiment is made must be brought to some standard temperature, or the differences of density caused by difference of temperature must be known by previous experiments, and allowed for.

§ 33. Since, at temperatures above that of its maximum density, water expands by increase of temperature (that is, becomes lighter), it follows that a mass of hot water, when placed amongst cold water, will rise through the latter as long as the two remain unmixed, and, having reached the surface, spread itself thereon in a manner similar to the spreading of oil on the surface of water. This fact gives rise to certain currents in the sea, caused by the solar heat, similar to those previously described as taking place in the air. For reasons described in § 23, the water at the equator is heated more strongly than that at the poles. It expands and would rise up in a mountainous belt, girdling the earth at the equator, were it not at the same time drawn to the earth by its weight. The only way by which it can approach the centre of gravity of the earth, is by travelling towards the poles. This it accordingly does, gliding over the surface of the colder water, which latter supplies its place by passing from the polar regions in cold undercurrents towards the equator, there to be warmed, raised, and so forced into continual circulation.

Fig. 12.



It is to be noted that, while we are acquainted chiefly with the lower strata of the air, the higher strata of the sea are most familiar to us; so that while the chief winds we experience blow from the poles, the chief oceanic currents examined proceed from the equator; that is, they move northerly in the northern, and southerly in the southern hemisphere. The ocean does not, like the atmosphere, cover the whole surface of the globe. The motion of both the upper and under currents is broken by continents and islands; their direction is changed; and sometimes they are so dispersed as to be entirely lost.

§ 34. One of the chief of these currents takes its rise in the Gulf of Mexico and West-Indian Archipelago. The water heated in this semitropical sea cannot proceed at once due north, but is forced by the contour of the land along the coast of North America. It spreads as it goes, the winds which blow over it are warmed, so that its influence is felt throughout the North Atlantic Ocean:—to the west, in Newfoundland and Greenland; in the middle, in Iceland; to the east, in Ireland and the west coast of Scotland. The climates of these countries are thereby rendered more mild and moist than those of countries of corresponding latitudes protected by their position from the influence of the Gulf-stream, such as North Canada, Siberia, &c.

§ 35. *Expansion of solids.*—All solids expand on being heated*. But, like liquids, some expand more than others for the same increase of temperature; and the same solid expands to different amounts if the temperature is different at which it receives the same increase of temperature. With regard to the latter fact, it is generally the case that if two equal masses of the same solid, the one hotter than the other, both receive the same increase of temperature, the hotter one will expand most. The volumes of solids are less influenced by change of temperature than those of liquids, and the volumes of liquids generally less influenced than those of gases.

§ 36. *Linear expansion of solids.*—If bars of equal lengths of the following solids be heated from the freezing- to the boiling-point of water, they increase in length as follows:—

---

* A notable exception to this law is furnished by an alloy of bismuth, tin, and lead, which, on being heated from the temperature of melting ice, first expands (to 44° C.), then contracts (to 69° C.), and finally expands until it melts.

		Length.	
1 length of zinc....	at the temperature of melting ice, becomes	1·002987	at the temperature of boiling water.
„ lead ..		1·002848	
„ tin		1·002173	
„ silver ..		1·001909	
„ copper..		1·001722	
„ gold ..		1·001466	
„ iron....		1·001235	
„ glass ..		1·000861	
„ platinum		1·000857	
„ deal ..		1·000380	

Whence it appears that, generally, the more difficultly fusible a metal is, the less does it expand by heat.

§ 37. The expansion of solids by heat is of great importance in many arts. A pendulum swings more slowly the longer it is. Hence a pendulum which beats seconds at one temperature will beat intervals greater than a second at a higher temperature, as in warmer weather. For many purposes it is sufficient to make the pendulum of some substance which expands but little by heat, such as glass, marble, or wood. But for more accurate timekeepers, the greater expansion of one metal is made to counterbalance the lesser expansion of a greater length of another.

The "gridiron" pendulum is constructed upon this principle (fig. 13). The iron pendulum-rod, *a*, is divided into two limbs, *b* and *e*; these are bent upwards at their lower ends and soldered to two upright rods of zinc, *d* and *c*; the zinc rods are joined at the top and soldered to another iron rod, *f*, which bears the bob, *g*. The expansion of the iron is that due to a rod of the length from *a* to *g*. The expansion of the zinc is that due to a rod of the shorter length, *d* or *c*. The expansion of the iron tends to depress *g*, that of the zinc to raise it. If properly adjusted, the one tendency exactly counterbalances the other, and *g* remains always at the same distance from *a*. Sometimes the same effect is produced by making the bob of the pendulum as a box, containing a cylindrical vessel of mercury (fig. 14). The mercury expands more rapidly than the pendulum-rod, and produces the same effect as the zinc in the gridiron pendulum. Both pendula are called, for obvious reasons, "compensating." Chronometers differ from watches in having similar arrangements applied to their balance-wheels.

Fig. 13.

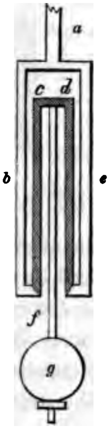


Fig. 14.

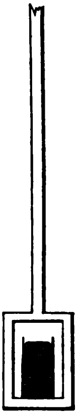
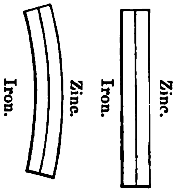


Fig. 15.

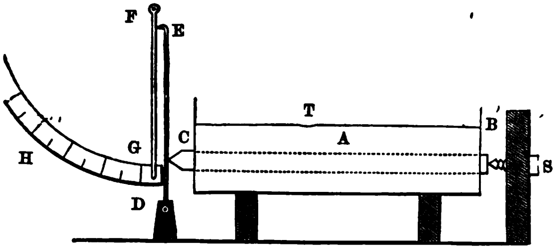


§ 38. The different rates of the expansion of iron and zinc may be shown by riveting two equal lengths together. When such a compound bar is heated, the zinc expanding most forces the bar to bend (fig. 15) in such a way that the zinc forms the convex side of the arch.

§ 39. The different linear expansions of different solids for the same increase, or those of the same solid for different increases of temperature, are shown in "Fergusson's Pyrometer" (fig. 16). A rod (A) of the solid, of known length, passes watertight through the end walls of a trough, T. One end, B of A, rests against the end of the screw S, working through a support. The other end, C of A, works upon the lever of the third order, D C E, of which the fulcrum is D; the other end of this lever works at E upon a second lever, F G, of the third order. The lower end of G, which is free to move, is before a graduated arc, H. It is clear that if

C advances a distance, X, E will advance a distance, $X\frac{DE}{DC}$, and G

Fig. 16.



will advance, $X\frac{DE}{DC}\times\frac{FG}{FE}$ (see Mechanics). Thus, if $DE=10\,DC$, and $FG=10\,FE$, then, for every advance of C, the advance of G will be 100 times as great. The instrument is used by screwing up S until G is opposite a fixed point on the scale, the rod being kept cold by filling the trough T with melting ice. If the ice be then exchanged for boiling water, the rod A expands. The end B cannot recede; the end C advances, and the index end G moves with exaggerated motion.

§ 40. The following are some of the more common consequences of the expansion of solids.

The equality in the expansions of platinum and glass make it possible to fuse glass upon platinum, without danger of subsequent separation on cooling. If glass be softened, a platinum wire may be thrust through it in such a manner as to form air-tight contact when cold. If an iron or copper wire be treated in the same way, it will shrink more rapidly than the glass, and crack away on cooling.

Allowance must be made for the expansion of the iron of bridges and similar structures, lest by alternation of temperature it may injure the masonry, which is not so affected by temperature.

Nails driven into bricks or mortar become loosened in cold weather, and gradually work themselves out.

The official standard of length (the yard) varies with the temperature. In order that its length may be the same, it must be brought to the same temperature—say, that of melting ice.

The force exerted by solids on expansion by heat and the equal force which they exercise on contraction by loss of heat, is enormous. But the amount of movement is so small, that this force can only be applied in the arts in a few cases.

The rivets used in joining boiler-plates are used red-hot, partly for the sake of convenience in hammering out their heads, but partly because on cooling they drag the plates together by their contraction with immense force.

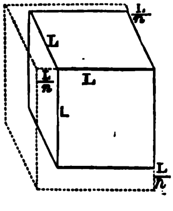
The tire of carriage-wheel is made a little smaller than the wheel. On making it hot it passes over the wheel; on cooling, it contracts and binds the wheel together. Metallic collars are in the same way "shrunk" on to bodies.

§ 41. Many solids, at the moment of becoming so from the liquid state, expand considerably, and also with great force. Thus ice, as it is formed, swells very considerably and with such force as to burst water-pipes, and even bomb-shells.

Type-metal, a mixture of lead and antimony, also swells at the moment of solidification from the melted state, and, in doing so, forces itself into the type-mould so perfectly as to produce a sharp and clean casting, which is necessary for clear printing.

§ 42. Many crystalline solids expand unequally in different directions, so that a change of temperature produces change of shape.

Fig. 17.



§ 43. *Expansion of solids by volume.*—If a solid rod of length L expands $\frac{1}{n}$th of its length for a given rise of temperature, becoming $L+\frac{L}{n}$, it follows that a cube of the same matter, each of whose edges has the length L, will expand equally in three directions. If V_1 be the volume of the cube, each of whose edges is L, then $V_1=L^3$. If, after heating, L becomes $L+\frac{L}{n}$, then, to find V_2, the increased volume, we have

$$V_2=\left(L+\frac{L}{n}\right)^3$$
$$=L^3+3L^2\frac{L}{n}+3\frac{L^2}{n^2}L+\frac{L^3}{n^3}.$$

If, as is always the case with solids, n is a very large number, or $\frac{1}{n}$ very small, the third and fourth terms of this value may be neglected, and we have very nearly

$$V_2=L^3+3\frac{L^3}{n}$$
$$=V_1+3\frac{V_1}{n},$$
$$V_2-V_1=3\frac{V_1}{n};$$

or the cubic increase of size is three times the linear.

CHAPTER IV.

THERMOMETERS.

§ 44. Instruments for measuring the temperature of bodies are called *Thermometers* (heat-measurers) or *Pyrometers* (fire-measurers). The latter are employed for determining very high temperatures, as those of furnaces, the temperatures of melting metals, &c.; the former are used for the measurement of the lower ranges of temperature.

§ 45. Since all bodies* expand by heat, it is clear that if we take a fixed quantity of any substance at any temperature, and accurately measure its size, we are sure that whenever it has the same size it will have the same temperature*. When it has a larger size it must have a higher, and when a smaller, a lower temperature.

---

* Excepting water at a certain temperature (§ 31), and an alloy of bismuth, tin, and lead (§ 35, note).

§ 46. Since (for the same increase of temperature) gases, as a rule, expand more than liquids, and liquids more than solids, it follows that a mass of gas of a given size will, by its change of size, form a more accurate and sensitive index of temperature than a mass of liquid or solid of the same size.

§ 47. *Air-thermometers* are used for determining sudden and slight changes of temperature. The arrangement of an air-thermometer has been described (§ 20, fig. 4). It is essential to the action of such a thermometer, that the surface of the liquid in the vessel A (see fig. 4) should be exposed to the air. The pressure of the atmosphere, however, is continually varying, both at the same place at different times and at different places at the same time. (See Natural Philosophy, Pneumatics.)

Consequently, even when the temperature remains the same, a diminution of the atmospheric pressure will cause a descent of the liquid in the stem of the instrument, by relieving the air in B of a part of the pressure which is compressing it; that is, such a diminution will produce the same effect as though the air in the upper bulb had undergone expansion by heat. For this reason such a thermometer cannot be used for comparing temperatures at different times or places, unless the variation in the atmospheric pressure, as measured by the barometer, be ascertained and allowed for.

§ 48. Leslie's "differential thermometer" consists of two glass bulbs, A and B (fig. 18), containing air, and connected together by a narrow tube, C, bent twice at right angles, containing mercury or some coloured liquid. The upright proportions of C carry scales. The whole being closed, the changes of barometric pressure are without influence upon the volume of air in either of the bulbs. But if one of the bulbs only, as A, be warmed, the air in it expands, forces down the liquid in the corresponding limb of C, and forces the liquid to rise in the opposite stem, thereby compressing the air in the bulb B. The inverse takes place if B be warmed while A is kept cool. Or if both bulbs be warmed, but one more than the other, the air most warmed will expand most, and the *difference* of temperature will be shown by the depression of the liquid in the stem of the bulb which is most warmed. If both bulbs be equally warmed, no motion of the liquid takes place, because equal forces of expansion act in opposite directions. Such a differential thermometer may be used, for instance, to compare the heat of the hand of a sick person, with that of the hand of one in health.

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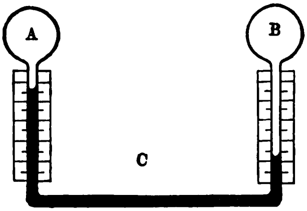
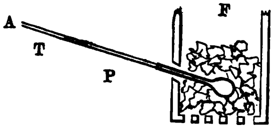
* In the case of gases, provided that the pressure upon it is the same.

Fig. 18.



§ 49. Air-thermometers may also be used as pyrometers in measuring the heat of furnaces. For this purpose (fig. 19) a flask of platinum, P (a difficultly fusible metal), is fastened to a very narrow glass tube, T, open at A. Both flask and tube being full of air, the former is placed in the furnace F, whose temperature is to be measured. The air in P expands, and the excess escapes by A. When the flask P has got as hot as the furnace can make it, the end A is closed by the blowpipe, and the flask is removed from the furnace. When cold, the end of A is broken off under mercury, and the quantity of mercury which thereupon enters the tube T and the flask P, measures the temperature to which the latter has been exposed.

Fig. 19.

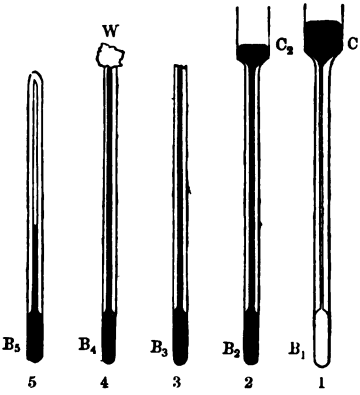


§ 50. The expansion of solids is also used for the measurement of very high temperatures—that is, for pyrometry. "Daniell's pyrometer" consists of a bar of platinum standing in a vertical position in a hole in a block of earthenware. The top of the platinum bar touches a plug of earthenware which rests upon the platinum and projects out of the hole. The plug is made to move with difficulty. The platinum, on expanding in the furnace, pushes up the plug of earthenware, which remains raised when the pyrometer is removed from the furnace. The degree to which the little plug has been pushed up is exactly measured (by applying it to the shorter arm of a lever), and gives comparatively the heat of the furnace.

§ 51. *Liquid thermometers* are those most often used for the measurement of all temperatures not exceedingly high. Two liquids are almost the only ones used in thermometers, namely, spirits of wine and mercury. Spirits of wine or alcohol cannot be frozen, and is therefore used to measure exceedingly low temperatures; but it easily boils, and is therefore useless for high ones. Mercury, on the other hand, can be frozen by severe cold; but it boils only at a very high temperature. Mercury, moreover, has the great advantage of great cohesion to itself, and little adhesion to glass; hence its surface is always sharply defined, and the mass of mercury unbroken. It will be sufficient to describe the construction of the mercurial thermometer.

§ 52. *Mercurial thermometer.*—A glass tube is formed having an exceedingly fine (capillary) bore of uniform capacity throughout. The shape of the bore in section is advantageously that of a slit; and its uniformity is tested by seeing whether a little mercury introduced into it always occupies the same length, to whatever part of the tube it is moved. Upon one end of such a tube, a cup, C_1, is blown, and upon the other a bulb, B_1, of less capacity than the cup (fig. 20, 1). More pure dry mercury is poured into the cup C_1 than is sufficient to fill the bulb B_1. The mercury does not descend into B_1 on account of the air in B_1, and because of the narrowness of the tube. This stage is seen in 1. The bulb B_1 is warmed, the air in it expands, and some of it escapes and bubbles through the mercury in C_1. On cooling B_1 some mercury follows the shrinking air, and drops into B_1. Heat is then applied to B_1 sufficient to boil the mercury in it. The vapour of mercury drives before it all the air in the bulb and stem, and

Fig. 20.



forces it through the mercury in C_1. On withdrawing the flame from B_1, the vapour of mercury condenses; and the atmospheric pressure forces the mercury in C_1 down the stem, until the bulb B_1 is completly filled. This is shown in 2. The cup C_2 is then cut off, as in 3. The bulb B_3 is then again heated as high as the temperature to which the thermometer has subsequently to be exposed. The excess of mercury as it expands, drops off from the end of the tube. When no more is expelled, some hot wax, W, is dropped upon the open end, so as to close it completely, 4. The mercury now on cooling shrinks; and since no air can enter, the bore of the stem above the mercury is a vacuum. Finally, the end of the tube below the wax is softened and closed; this the pressure of the air upon the sides of the empty stem assists.

§ 53. To graduate the thermometer, it is necessary that the height of the mercury, at at least two fixed and constant temperatures, should be known. For reasons which will be explained in §§ 85–96 under latent heat, the temperature of melting ice is constant, and is the same as that of the water which it forms on melting. Hence, if coarsely pounded ice be allowed to melt, it will remain continually of the same temperature as long as any ice remains unmelted. Further, for a similar reason (also described under latent heat, § 85) boiling water has always the same temperature, and the same as that of the steam which is formed from it *.

§ 54. The thermometer (5, fig. 20) is plunged into melting ice, and the point to which the mercury sinks in the stem is marked upon the glass. It is then plunged into boiling water, and the point to which the mercury rises is again marked. We know now that whenever the mercury stands at the lower point, its temperature is that of melting ice; and whenever at the higher, it is that of boiling water. When it stands between the two, it is of intermediate temperature. The glass stem between the two fixed points is divided into equal parts, called degrees. In different countries the number of these divisions is different. There are three principal systems of division. The simplest, and that most frequently used for scientific purposes, is the *Centigrade* or Celsius. On the Centigrade thermometer the temperature of melting ice is called zero (marked 0° C.); the temperature of boiling water is 100 (marked 100° C.). The intervening space is divided into 100 equal divisions or degrees. In *Réaumur's* thermometer, which is in popular use in Germany and Russia, the temperature of melting ice is 0°, that of boiling water is 80 (marked 80° R.), and there are 80 equal divisions or degrees between the two. On the *Fahrenheit* scale, the melting-point of ice is marked 32° F., and the boiling-point of water 212° F.; there are therefore 180 degrees between them. The Fahrenheit thermometer is in popular use in England.

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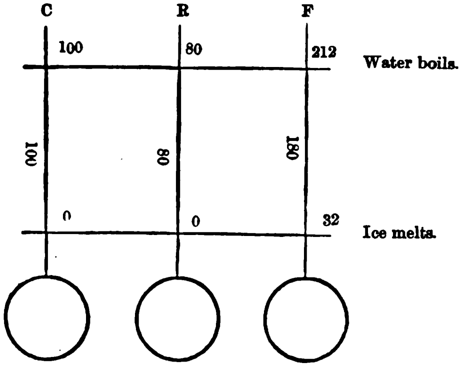
* The influence of pressure not considered. How this affects the temperature at which a liquid boils, will be seen under Ebullition, § 138.

CHAPTER V.

RELATION BETWEEN THE THERMOMETRIC SCALES IN COMMON USE.

§ 55. The relation between the Centigrade, Réaumur, and Fahrenheit scales is seen in fig. 21, where the three thermometers are supposed to be of exactly the same size.

Fig. 21.



C. graduated according to the Centigrade scale.
R. „ „ „ Réaumur „
F. „ „ „ Fahrenheit „

It is clear that the length of a degree on the C. scale is to the length on the R. scale inversely as 100 is to 80, or directly as 4 is to 5. The length of a degree C. is to the length of a degree F. as 180 to 100, or as 9 to 5; and the length of a degree R. is to the length of a degree F. as 9 to 4.

If, therefore, the mercury stands at a certain number of degrees C., and we wish to know what it is on the R. scale, we must take a less number of the larger R. degrees, and indeed a number bearing the inverse proportion to the number C. that the size of the R. degree bears to the size of the C. degree; or

$$\frac{\text{No. of degrees R.}}{\text{No. of degrees C.}}=\frac{4}{5}.$$

Example 1.—What temperature R. corresponds to 30° C.?

Answer. $30 \times \frac{4}{5} = 24$:

which is thus written, 30° C$=24^\circ$ R.

Moreover to convert temperatures R. into temperature C. we must multiply the number of degrees R. by $\frac{5}{4}$.

Example 2.—What temperature C. corresponds to 14° R.?

Answer. $14 \times \frac{5}{4} = 17{\cdot}5$,

or 14° R.$=17^\circ{\cdot}5$ C.

A similar transformation from the C. and R. to the F. scale would apply if the F. scale like the others commenced at zero. But a temperature of, say, 2 degrees F. above the melting-point of ice is not 2° F., but $2^\circ + 32^\circ$ F., and so on for other temperatures. Therefore, in transforming C. into F., after converting the number of degrees C. into the corresponding number F., by multiplying by $\frac{9}{5}$, we must add the constant 32° F. in order to get the actual temperature F.

Example 3.—What temperature F. corresponds to 42° C.?

Answer. $42 \times \frac{9}{5}$ above 32° F.,

that is, $42 \times \frac{9}{5} + 32^\circ$ F.,

or 42° C.$=107^\circ{\cdot}6$ F.

Similarly in converting R. into F.

Example 4.—What temperature F. corresponds to 21° R.?

Answer. $21 \times \frac{9}{4} + 32$,

or 21° R.$=79^\circ{\cdot}2$ F.

To convert F. temperatures into C. temperatures, it is (for a similar reason) necessary to subtract from the former the constant 32, so as to reduce the F. scale to the same starting-point before multiplying by the inverse sizes of the degrees.

Example 5.—What temperature C. corresponds to 200° F.?

Answer. $(200-32)\frac{5}{9}$,

or 200° F.$=93^\circ{\cdot}3$ C.

And so in converting F. temperatures into R. temperatures.

Example 6.—What temperature R. corresponds to 52° F.?

Answer. $(52-32)\frac{4}{9}$,

or 52° F$=8^\circ{\cdot}8$ R.

The following Table of formulæ contains all possible cases of transformation of any temperature expressed on one scale to any other scale:—

n° C. $=\frac{4}{5}n^\circ$ .... R.
n° R. $=\frac{5}{4}n^\circ$ .... C.
n° C. $=\frac{9}{5}n^\circ+32^\circ$ .... F.
n° R. $=\frac{9}{4}n^\circ+32^\circ$ .... F.
n° F. $=\frac{5}{9}(n^\circ-32^\circ)$ .... C.
n° F. $=\frac{4}{9}(n^\circ-32^\circ)$ .... R.

§ 56. The zero Fahrenheit is 32° F. below the melting-point of ice. Equal divisions on the glass are carried both above the boiling-point of water and below that of melting ice. The degrees of heat below zero are called negative, and a minus sign is prefixed to them. Thus mercury freezes at -39° C. or $-38^\circ\!\cdot\!2$ F., or $-31^\circ\!\cdot\!2$ R., &c*.

§ 57. The following Table gives some idea of the range of some natural and artificial temperatures.

	Temperature, C.
Supposed temperature of stellar space ..	— 142
Greatest artificial cold	— 140
Greatest observed natural cold	— 49
Mercury freezes	— 39
Mixture of snow and salt	— 20
Water freezes or ice melts	0
Maximum density of water	+ 4
Heat of human blood	36·6
Water boils or steam condenses (at 760 millims.)	100
Mercury boils	360
Supposed heat of the sun	1761
Highest heat of furnace	1804

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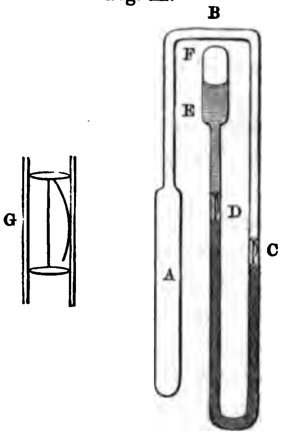
[*] The student should practise conversion of both + and — degrees of temperature from each scale to the other two until he is familiar with the use of the above formulæ.

Still higher temperatures are obtained by the burning-glass, by the oxyhydrogen blowpipe (see Part II.), and by the interruption of the galvanic current. But neither extreme heat nor extreme cold can be measured with accuracy, because it is not known whether at such temperatures the substances used in the pyrometers or thermometers obey exactly the same law of expansion.

§ 58. *Registering thermometer; maximum and minimum thermometer.*—For some purposes, especially in meteorology, we wish to know the highest or lowest temperature (or both) which has been reached during a certain time. This is done by making the liquid in the thermometer leave a mark at the extreme points which it has reached. Fig. 22 shows the construction. The expanding liquid is alcohol contained in the vessel A. The vessel A, with its twice bent tube B, is full of alcohol as far as C. From C to D the lower bend is filled with mercury. Above D there is alcohol again; and the other end E, which is widened into a bulb, is also partly filled with alcohol, but part, F, is empty. When the temperature of the whole rises, the alcohol in A expands, forces down the mercury in C, and forces up the mercury in D. Resting upon the mercury inside the tube, there is at C and at D a little plug, consisting of two glass beads joined by an iron wire, and made to slide with some difficulty in the tube by means of a little glass thread springing against the side of the tube. This contrivance is shown enlarged at G. If the position as represented in the figure be that at the maximum temperature: when the alcohol in A shrinks, the mercury in C will follow it and push up the plug C, while the plug D will be left at its maximum height by the falling mercury. Inversely, when the alcohol expands the mercury sinks from below C, leaving it, but it pushes up the

Fig. 22.



plug D. The stem C is accordingly graduated from above downwards, the stem D from below upwards. In order to set the instrument after use, the plugs are moved in the tubes so as to touch the mercury, by means of a magnet, which attracts the iron wire connecting the beads.

CHAPTER VI.

Difference between Temperature and Quantity of Heat.

§ 59. *The temperature* of a body, called sometimes, but improperly, its sensible heat, is so elementary a notion as to defy direct definition. Any two bodies of different temperature in contact (as indeed also apart, see Radiation) will tend to approach the same temperature intermediate between them. Thus all bodies in the same room, unless some of them are subject to special influences, have the same temperature. Two similar coins laid on the table will, after a time, have the same temperature. If they are both held at the same distance from the fire they will rise equally in temperature, so that, though both warmer than before, they will have the same temperature as one another. The two coins will in both cases *feel* equally cool or equally warm. Hence the term "sensible heat." But two bodies of the same temperature may, to the sense of touch, *appear* to have different temperatures. (See Conduction.) Thus a copper coin at 0° C. will feel very cold; copper filings at the same temperature will not feel so cold. The hand in the second case is not cooled so much, does not lose so much heat as in the first. And it is only the amount of gain or loss of heat by the hand which determines the use of the terms hot, warm, cool, cold (See § 4). Sensible heat is therefore not so appropriate an expression as temperature.

§ 60. The temperature of a body is shown and measured by the expansion or contraction of known volumes of other bodies placed in contact with the first—that is, by thermometers. One body has a higher temperature than another when it causes the mercury in a thermometer placed in contact with it to stand at a higher level than the second body does; so that, if a thermometer be placed in succession in contact with two indefinitely great quantities of two substances, the one which causes the mercury to stand highest in the thermometer has the greatest or highest temperature. Temperature may be called the intensity of heat.

§ 61. It is clear that if two equal masses of the same matter have the same temperature, there is twice as much heat in the two together as in either of them singly. The *quantity* of heat in a given kind of matter at any given temperature varies therefore as its mass, weight, or volume.

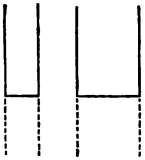
§ 62. It is found by experiment that if two equal masses (weights) of different kinds of matter at the same temperature receive equal amounts of additional heat, though they both may rise in temperature they seldom rise equally in temperature. The one has a greater *capacity for heat* than the other; the accession of the same quantity of heat does not raise its temperature so much.

§ 63. Thus, if 1 lb. of mercury and 1 lb. of water at the same temperature be held over the same flame of a candle for the same time, the mercury will get hot much more quickly than the water, and will constantly show a higher temperature to the thermometer. It is true that the 1 lb. of mercury is much smaller in bulk than the 1 lb. of water; but this is not the reason of its more rapid heating. For if 1 lb. of oil, which has a greater volume than 1 lb. of water, be exposed under the same conditions, it too will rise more rapidly in temperature than the water, and continually have a higher temperature. Water is said to have a greater *capacity* for heat than either mercury or oil. The same quantity of heat entering into it affects its temperature less. Or, what comes to the same thing, in order to raise equal weights of water and of mercury or oil from one temperature to the same higher one, more heat must enter the water than enters the mercury or oil.

§ 64. Inversely, if the same weights of water, mercury, and oil have the same temperature, and the same quantity of heat be withdrawn from each, the water will be least affected, and its final temperature will be above that of the others. And if the temperatures of all three equal weights be reduced from any one the same temperature to any other the same temperature, more heat must be withdrawn from the water than from either of the others.

§ 65. The relation between the ideas temperature, capacity for heat, and quantity of heat may be conveniently illustrated by comparison with a well of water. Let there be two cylindrical wells (fig. 23) of different capacities (sectional areas) containing water.

Fig. 23.



The height of the water represents the *temperature*. The capacity of the well (that is, its sectional area) represents the *capacity* of the body for heat. The quantity of water in the well represents the *quantity* of heat in the body.

Thus we have the following parallel cases:—

The water in both wells stands at the same height.
The temperature of both bodies is the same.

On adding or subtracting the same amount of water to or from both wells, the height of the water in the well of greater capacity is less raised or depressed than in the well of less capacity.

On adding or subtracting the same amount of heat to or from both bodies, the temperature of the body of greater capacity for heat is less raised or depressed than that of the well of less capacity.

More water must be added to, or taken from, the well of greater capacity, to alter the height of its water a given amount, than is the case with the one of less capacity.

More heat must be added to, or taken from, the body of greater capacity, to alter its temperature a given amount, than is the case with the body of less capacity.

§ 66. It is self-evident that the entire quantities of heat in two bodies of the same temperature and of equal masses are proportional to their capacities for heat, just as the entire quantities of water in the two wells are proportional to their capacities if it stands at the same height in both. The total or absolute quantity of heat in a body is never known, because the state of absolute cold is not known. Returning to our illustration, the depth of the well is not known.

§ 67. Quantity of heat may be measured through its cause or through its effect. Thus, by the first means, a given weight of charcoal, burning completely in the air, gives out a certain invariable quantity of heat; a given amount of mechanical force, expended in overcoming friction, gives rise to a definite quantity of heat; the sun at a given altitude, shining on a given surface, gives it a fixed quantity of heat, &c. But quantity of heat is most conveniently measured by its effect.

§ 68. If a given weight of a given substance at a given temperature be heated to another fixed temperature, or through a certain number of degrees, the amount of heat employed may be taken as a unit of heat. The most convenient unit to employ is the amount of heat necessary to raise a gramme of water at 0° C. to 1° C. If twice the heat be applied, the gramme attains the temperature of 2° C., and so on*. Further, to raise the temperature of 2 grammes of water 1°, twice the heat must be added; and generally to raise m grammes of water n degrees, $m \,.\, n$ units of heat must be employed. The number of units of heat necessary to raise a given weight of any substance a given number of degrees is of course directly proportional to the capacity of the body for heat. Using the former illustration of a well, a unit of heat may be compared to a bucket of water.

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* This is sufficiently nearly the case for our present purpose. The water would really be heated to an inappreciably small fraction of a degree below 2° C., as we shall subsequently see.

CHAPTER VII.

SPECIFIC HEAT.

§ 69. If the proportion between the quantity of heat necessary to raise a given weight of one substance, A, through a number of degrees be compared with (divided by) the quantity of heat necessary to raise the same weight of another substance taken as a standard, B, through the same number of degrees, the *Specific Heat* of the substance A is obtained. The substance used as a standard of comparison is almost universally water.

§ 70. It follows from § 68 that the specific heat of a body is got by raising equally its temperature and that of an unequal quantity of water by adding the same quantity of heat to both, and dividing the quantity of water by that of the body; and :—

§ 71. By adding the same quantity of heat to equal weights of the body and of water, and dividing the number of degrees gained by the water by the number gained by the body.

§ 72. It must be borne in mind that specific heat is not heat, but number—just as specific gravity is not weight, but number. Both of them are quotients. It is also evident that the specific heats of two bodies are proportional to their capacities for heat.

§ 73. Since the heat lost by a body on cooling is exactly equal to the heat it had gained on being heated through the same number of degrees, the heat lost by the warmer of two bodies of different temperature in contact is exactly equal to the heat gained by the cooler.

§ 74. If one of them be the standard body, water, the specific heat of a body is at once found by taking a known weight of the body at a known temperature and bringing it into contact with a known weight of water at another known temperature, and observing the temperature which they both have when the warmer has been cooled and the cooler warmed.

§ 75. Thus if 10 oz. of water at 0° C. be agitated with 10 oz. of water at 100° C., the result will be 20 oz. of water at 50° C.

The one 10 oz. has lost 50° of heat, the other 10 oz. has gained 50°. The specific heat of water is by definition unity $\left(=\frac{50}{50}\right)$.

§ 76. If now 10 oz. of water at 100° C. be agitated with 10 oz. of mercury at 0° C. until they both have the same temperature, that temperature will be found to be 96°·8 C.; or the heat which on leaving the 10 oz. of water only reduced its temperature 3°·2 C., has been sufficient to raise that of an equal weight of mercury 96°·8 C. Hence the specific heat of mercury

$$=\frac{3^{\circ}\cdot 2}{96^{\circ}\cdot 8}=0\cdot 033.$$

§ 77. If unequal quantities of the substance and water are employed, as is most frequently the case, the above ratio of loss and gain of the respective temperatures must (as appears from §§ 68 and 70) be multiplied by the ratio of the weights used. In general terms, let

t_1 be the original temperature of the water,
w_1 be the weight of the water,
t_2 be the original temperature of the substance,
w_2 be the weight of the substance,
t_3 the final temperature of both.

Then, supposing the body to be hotter than the water originally,

$$\text{specific heat}=\frac{t_3-t_1}{t_2-t_3}\times\frac{w_1}{w_2}.$$

Example.—4 lb. of water at 20° C. are mixed with 6 lb. of a liquid at 72° C. The mixture has the temperature of 23° C. Required the specific heat of the liquid.

Here

$$t_1=20^{\circ}\text{ C.},\ w_1=4\text{ lb.},\ t_2=72^{\circ}\text{ C.},\ w_2=6\text{ lb.},\ t_3=23^{\circ}\text{ C.}$$

$$\text{Specific heat}=\frac{23^{\circ}-20^{\circ}}{72^{\circ}-23^{\circ}}\times\frac{4\text{ lb.}}{6\text{ lb.}}$$
$$=0\cdot 041.$$

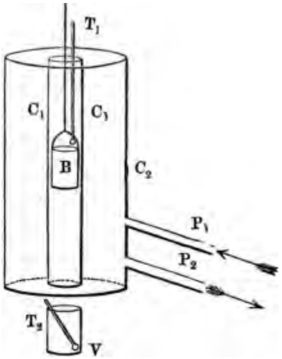
CHAPTER VIII.

CALORIMETERS.

§ 78. The determination of the specific heat of bodies is called "calorimetry." Special instruments called "*calorimeters*" are constructed for exact determinations. The above (§§ 73–77) is a simple means of determining roughly specific heat by what is called the method of mixture. The same principle is most frequently employed in calorimeters, but certain precautions are used to increase the accuracy of the result.

The following is a brief description of one form of calorimeter applicable to the determination of the specific heat of many solids and liquids. A known weight of the substance is hung in a little basket, B, fig. 24, of brass wire. If the substance be a liquid or a solid which is influenced by water, it is enclosed in a thin glass tube and placed in the basket. The basket is hung in the middle of a double copper cylinder C_1 C_1 C_2 C_2, between the walls of which a current of steam at 100° C. is made to circulate by means of the pipes P_1 and P_2; so that the basket and its contents are in a cylindrical chamber between whose double walls steam of constant temperature is continually circulating. The consequence is that the substance in the basket, without having been actually in contact with the steam, yet acquires, after a time, exactly its temperature. This is seen to be the case by reading the thermometer T_1, whose bulb touches the basket and whose stem passes through a cork closing the top of the inner cylinder. There is then slipped beneath the basket a little vessel of polished brass, V, containing a known quantity of water at a known temperature, as marked on the second thermometer, T_2. The basket, B, is immediately lowered

Fig. 24.



rapidly into the water in V, which is instantly slipped away. The basket containing the substance is stirred up in the water, and gives it a portion of its heat. The thermometer, T_2, rises and shows how much heat the water has gained. Various other precautions and corrections have to be observed, which need not be mentioned here.

§ 79. If the substance be acted upon by water, turpentine may be sometimes used instead in V. By this means the capacity for heat of the substance compared with that of turpentine is in the first instance found. But if the capacity for heat of turpentine compared with that of water (that is, its specific heat) be also found, the capacity for heat of the substance compared with that of water (that is, its specific heat) is got from the simple proportion:—If

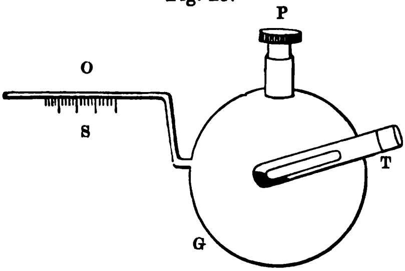
$$\frac{\text{Capacity for heat of substance}}{\text{Capacity for heat of turpentine}}=a,$$

$$\text{Specific heat of turpentine}=b,$$

then $$\text{Specific heat of substance}=a\,b.$$

§ 80. Another form of calorimeter is based upon the measurement of the expansion of a known volume of mercury of a given temperature when it has received the heat which a known weight of the substance loses on cooling. A glass globe, G (fig. 25), with its attached tube S is completely filled with mercury as far as the mark O on the scale borne by the tube S. This is effected by adjusting a screw-plug, P, which works tightly through the upper part of the globe. At T a little tube of thin glass is fused

Fig. 25.



into the globe, with its closed end in the globe and its open end outside. The tube T also contains a little mercury. The substance previously weighed and heated to a known temperature (say, 100° C.) is introduced into T, either in the free state or enclosed in a smaller tube of very thin glass. As the substance gives up its heat to the mercury, the latter expands and advances along the tube S. Bodies of the greatest specific heats will of course cause the greatest expansion.

§ 81. It is also possible to determine roughly the specific heat of a body by burying a piece of it of known weight and known temperature in a dry cavity of a piece of melting ice. The quantities of ice melted (that is, the quantities of water formed) will be in the proportion of the specific heats of the bodies experimented on.

§ 82. The specific heats of gases and vapours are found by passing known volumes (and therefore known weights) of them at a known temperature through a spiral worm of thin metal traversing a vessel containing a known weight of water at a known temperature. If the temperature of the escaping gas be found, all the necessary data for determining the specific heat of it are in our possession.

§ 83. The following Table shows the specific heats of a few substances, gaseous, liquid, and solid. It will be noticed that one and the same substance has different specific heats according as it is in the gaseous, liquid, or solid state.

Specific heat of water = 1.

Gases.		Liquids.		Solids.	
Hydrogen	3·4090	Mercury	0·0333	......	0·0319
Nitrogen	0·2438	Phosphorus	0·2120	......	0·1887
Oxygen	0·2175	Sulphur	0·2340	......	0·2026
Air	0·2374	Lead	0·0402	......	0·0314
Carbonic acid	0·2163	Alcohol	0·6150	Gold	0·0324
Carbonic oxide	0·2450	Oil of turpentine	0·4670	Silver	0·0570
Chlorine	0·1210	Terchloride of phosphorus.	0·2092	Platinum	0·0324
Bromine	0·0555	....	0·1060	......	0·0843

§ 84. The specific heat of a substance in the solid state is increased with its temperature.

At its temperature of fusion, a further sudden increase of specific heat almost always takes place.

On being further heated as a liquid, its specific heat further increases.

On being converted into a vapour, its specific heat is suddenly diminished.

The specific heat of the substance in the gaseous or vaporous state is the same at all temperatures.

Thus :—

	Between.		Mean specific heat.
Ice	−70° C. and 0° C.	=	0·474
	−20 „ 0	=	0·504
Water	at 0	=	1·000
	at 100	=	1·130
Steam		=	0·480

CHAPTER IX.

LATENT HEAT.

§ 85. If heat be gradually applied to a mass of very cold ice (say, at −10° C.), the following changes are observed. At first it gets warmer, until the entire mass has the temperature of 0° C. It then commences to melt; but during its melting (that is, as long as any ice remains), both the remaining ice and the liquefied ice or water maintain precisely the same temperature of 0° C. As soon as all the ice has disappeared (the heat being continually applied), the water gradually rises in temperature until it reaches the temperature of 100° C. It then commences to boil; but during its boiling (that is, as long as any water remains), both the remaining water and the vaporized water or steam maintain precisely the same temperature of 100° C. As soon as all the water has disappeared (the heat being continually applied), the steam gradually rises in temperature and may attain any temperature. There are therefore two conditions of the substance (namely, as ice at 0° C. and as water at 100° C.) when accession of heat does not produce rise of temperature but change of physical state—namely, ice at 0° C. to water at 0° C., and water at 100° C. to steam at 100° C.

The heat which enters the ice at 0° C. to form water at 0° C., and the heat which enters the water at 100° C. to form steam at 100°, is said to become *latent* or hidden, because it neither affects the sense of touch nor the thermometer. In the first case the heat becomes latent in the water at 0° C., in the second it becomes latent in the steam at 100° C. Such heat has also received the better names of heat of liquefaction in the first case, heat of vaporization in the second.

§ 86. Inversely, if heat be continuously withdrawn from a quantity of hot steam, say, at 110° C., the first effect will be to cool the steam; this will go on until the temperature of the steam is reduced to 100° C. On continuing to withdraw the heat (as by contact with a cold body) the steam will begin to condense; but both the remainder of the steam and the water formed from it will maintain the same temperature of 100° C. as long as any steam remains uncondensed. On continuing to withdraw the heat from the water at 100° C., it will gradually fall in temperature until it reaches 0° C. If heat be still withdrawn, the water no longer sinks in temperature, but begins to freeze. As long as any water is left unfrozen, both the residual water and the ice formed from it will maintain the same temperature of 0° C. As soon as all the water is frozen, if the abstraction of heat be continued, the ice may be cooled to any degree.

§ 87. The heat withdrawn from the steam at 100° C. to convert it into water at 100° C. is the same in quantity as the latent heat of the steam, and may be considered as the identical heat which entered the water at 100° C. to convert it into steam at 100° C. And, in like manner, the heat which is withdrawn from the water at 0° C. to convert it into ice at 0° C. is the same in quantity, and may be considered identical with the latent heat of the water—that is, with the heat which entered the ice at 0° C. to convert it into water at 0° C.

§ 88. All solids absorb heat on liquefaction, and all liquids give out heat on solidification. All liquids absorb heat on vaporization, and all vapours give out heat on condensation.

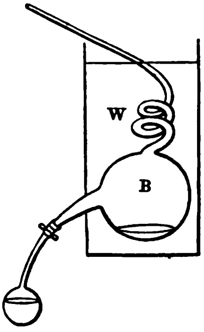
§ 89. The constancy of the temperatures of melting ice and of boiling water has already been applied to the determination of the fixed points on the thermometric scale (§ 54).

§ 90. The latent heat of a liquid may be determined by bringing a quantity of it just to the temperature at which it begins to solidify, and then bringing it into contact with a known weight of a solid at a lower temperature, and observing, 1st, how much of the liquid is solidified, and 2nd, how much the solid has increased in temperature; for it is clear that the heat withdrawn from the liquid to solidify it, *i. e.* the latent heat of the liquid, is equal to the heat acquired by the cold solid. Inversely, the latent heat of a liquid may be also found by bringing it to the solid form, taking a quantity of it at the temperature at which it just begins to melt, and immersing it in a known weight of a liquid at a higher temperature, and noting, 1st, how much of the solid is liquified, and, 2nd, how far the temperature of the warming liquid has fallen.

§ 91. It is evident that if, after the solid is melted in a warm liquid, the two liquids remain in contact until their temperature becomes the same, the warm liquid will have had not only to melt the solid, but to raise the resulting liquid from the temperature at which its melting took place to the temperature which both have finally. The correction necessary is known on knowing the capacity of the liquefied solid for heat. If the solid be in excess, so that when the two have attained the same temperature some of the solid remains unliquefied, and all the substances present have consequently the original temperature of the solid, no such correction is needed.

§ 92. The latent heat of a vapour is found by leading it through a worm surrounded by a known quantity of a colder liquid (generally water) until it ceases to be condensed—that is, until the temperature of the condensing liquid reaches that of the vapour. Fig. 26 shows such an arrangement. The liquid is boiled in the flask F. Its vapour mainly collects and condenses in the bulb B; the remainder condenses in the worm. On finding how much of the liquid in F has been boiled away, or, what is the same, how much vapour has been condensed, and on knowing the weight of the water which, while rising a certain temperature, has withdrawn the latent heat of the liquid vapour and condensed it, we can, as before, deduce the latent heat of the vapour, because the increased heat of the water is exactly equal to the latent heat of the vapour.

Fig. 26.



§ 93. The following are a few instances of the latent heats of liquids and vapours:—

Latent Heat.

Liquids.		Vapours.	
Water	79·2	Water	535
Melted Sulphur	9·4	Alcohol	202
„ Lead	5·4	Bromine	45
„ Zinc	28·1		
„ Bismuth	12·6		

§ 94. Of all vapours that of water has the greatest latent heat.

§ 95. Those liquids have the greatest latent heats whose corresponding solids have the highest melting-points.

§ 96. The latent heat of water is of great influence in nature, by equalizing the temperature of the earth, the sea, and the air. For if a portion of the sea be exposed to great cold, it freezes, giving heat out of its great store of latent heat. A continuance of the cold does not depress the temperature of the ice, but causes more to be formed. When the summer sun shines upon the ice, it does not warm it but melts it. Thus, in both cases, sudden changes of temperature are avoided, and the winds which blow from the polar regions are more uniform in temperature (see § 23). Rivers whose sources are on snow-covered mountains would cause disastrous floods in spring time, if the water at the moment of its formation did not absorb as latent heat a part of that given by the sun; for otherwise the whole of the snow would melt at once on receiving heat, the moment after its temperature rose to 0° C.

CHAPTER X.

LIQUEFACTION.

§ 97. *Liquefaction of solids.*—We have hitherto supposed the heat to be *applied* to the solid to produce liquefaction, and to the liquid to produce vaporization. If the solid be melted by any other means, in liquefying it seeks to obtain heat from surrounding objects. If it cannot do so it refuses to liquefy; so that when a solid liquefies by such means it absorbs heat or "produces cold."

§ 98. Many solids may be liquified by dissolving them in liquids; and some solids when brought together melt in order to mix, provided that their mixture is a liquid. In such cases heat is absorbed by the body undergoing liquefaction, and withdrawn for that purpose, if possible, from surrounding objects.

§ 99. "Freezing-mixtures" act on this principle. If equal weights of a solid body called nitrate of ammonium (see Part II.) and water, both at 10° C., be mixed, the nitrate of ammonium dissolves and becomes liquid; the mixture sinks in temperature to $-15^\circ{\cdot}5$ C. If two parts by weight of snow at 0° C. be mixed with one part of common salt at 0° C., a temperature of -20° C. is obtained. Again, mercury dissolves many metals, forming what are called "amalgams:" frequently a considerable fall of temperature attends the solution.

§ 100. Inversely, a liquid may sometimes be converted wholly or partly into a solid without the withdrawal of heat—as when a solid suddenly crystallizes out of a liquid. This is always accompanied by a sudden evolution of latent heat from the liquid.

§ 101. *Liquefaction of gases.*—When a gas simply dissolves in a liquid without uniting chemically with it (that is, without forming any new compound—Part II.), heat is evolved. Thus, when steam at 100° C. is passed over dry sugar, a syrup is obtained of a temperature above 100° C.

§ 102. When gases unite chemically with one another and form liquids, heat is always evolved; and when a gas unites chemically with a liquid, so as to form a new compound, heat is also evolved. In both cases the heat is due in part to the escape of the latent heat of the gas. Thus heat is given out when a gas (oxygen) unites with another gas (hydrogen) and forms a liquid (water). A gas, ammonia, dissolves in and combines with water, giving out heat.

Liquefaction of gases will be further considered in the next chapter.

CHAPTER XI.

EVAPORATION AND EBULLITION.

§ 103. At temperatures far below their boiling-points, but not at all temperatures, all known liquids in contact with gases or exposed to *vacuo* are found to give rise to vapour; that is, the surface of the liquid is converted into vapour and spreads out or diffuses into the gas or empty space above it. Such separation of a part of a liquid as a vapour is called *evaporation*. When the same takes place from a solid, it is called *volatilization*.

§ 104. The mechanical force which is thus exerted is called the *tension* or *elastic force* of the vapour of the body.

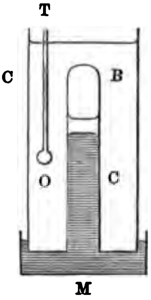
§ 105. The tension of the vapour of a body *in vacuo* may be very conveniently measured by introducing a little of it into the vacuum of the barometer. The mercury is then depressed, and the distance through which it is driven down is a direct measure of the tension of the vapour of the substance.

When a part of a body is thus converted into vapour, the cohesion of the body is overcome.

§ 106. We already know that the particles of a body are separated by heat, the body thereby expanding. When, therefore, the particles of a liquid are further removed from one another by heat, their cohesion as a liquid offers less resistance to the tension of the vapour. Accordingly it is found that the tension of a vapour in contact with the substance which gave rise to it increases with the temperature, and, according to the increased temperature, depresses further the barometric column.

§ 107. To show the increase of tension with temperature, a few drops of the evaporating body (suppose a liquid) (fig. 27) are introduced above the mercury, M, of a barometer, B. The barometer is enclosed in a glass cylinder, C, containing some transparent liquid, which may be heated. Thus, suppose the surrounding liquid is oil, of the temperature 0° C., and the mercury stands at 760 millims. in the barometer, B. On introducing into the barometic vacuum ice of the temperature —32° C., the mercury sinks 0·310 millim. As the oil is warmed (its temperature being ascertained by the thermometer, T), the mercury in B is forced lower and lower down by the ever increasing tension of the vapour of the ice (which is identical with the vapour of water, and is steam), until the ice melts. Thenceforth the vapour rises from water. The following Table shows in millimetres the elastic force or tension of the vapour at a few different temperatures:—

Fig. 27.



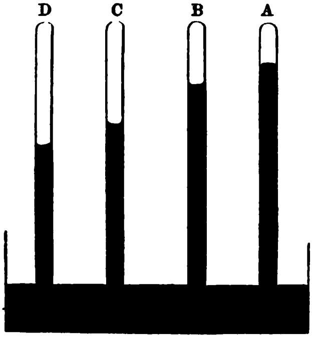
			millims.
At −30° C.	the mercury	sinks	0·365
−20	,,	,,	0·841
−10	,,	,,	1·963
0	,,	,,	4·600
+10	,,	,,	9·165
20	,,	,,	17·391
30	,,	,,	31·548
40	,,	,,	54·906
50	,,	,,	91·982
60	,,	,,	148·791
70	,,	,,	233·093
80	,,	,,	354·643
90	,,	,,	525·450
100	,,	,,	760·000

The tension therefore increases much more rapidly than the temperature.

§ 108. At 100° C., that is, when the water begins to boil, the tension of its vapour exactly counterbalances the pressure of the air; and the mercury in the barometer stands at the same level as that outside.

§ 109. The tension of the vapour of different substances at the same temperature is very different. This is seen on introducing different substances at the same temperature into a series of similar barometers (fig. 28).

Fig. 28.



Let the barometer A be empty.
In B let there be water.
„ C „ „ alcohol.
„ D „ „ ether.

It is found that the tensions of the different vapours are in the order, ether, alcohol, water—the mercury being depressed in this order. In the ordinary barometer itself there is a slight depression, due to the tension of the vapour of mercury. Mercury itself gives rise to a vapour which at ordinary temperatures is very slight, at 100° C. being only 0·003 millim., and at 200° C. being 1·930 millim.

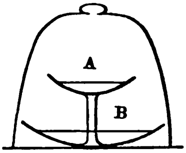
§ 110. The tensions of the vapours of different substances have not been minutely examined; but it appears that, of two substances, the one which boils at the lower temperature will have a vapour of the greater tension.

§ 111. If pressure be applied to the surface of a body which is giving off vapour, the tension of the vapour is opposed and checked; it may be altogether counteracted. The pressure of the atmosphere (15 to 16 lb. per square foot) is such an opposing force. On diminishing the pressure of the air on an evaporating surface, the evaporation is increased; and if the air be entirely withdrawn, as in the barometer-tube, the evaporation is as great as it can be at the given temperature. In the latter case, if the vapour as formed be withdrawn, fresh quantities of vapour will rise; and if it be continually withdrawn, a continuous evaporation of the liquid must ensue. The same takes place to a less extent if the withdrawal of the air in the first instance be incomplete—that is, if the vacuum formed above the liquid be imperfect.

§ 112. The conversion of a liquid into a gas is, as we know, always attended by an absorption of heat which becomes latent in the gas or vapour.

§ 113. Hence, if a little water in a shallow basin be placed under the receiver of an air-pump over another basin containing some substance eager to absorb water or its vapour, such as oil of vitriol, and the air be pumped out, the following effects take

Fig. 29.



place. The opposition to the tension of the vapour of the water being withdrawn or diminished by the total or partial removal of the air, the watery vapour rises from A and fills the receiver (fig. 29). A is the water, B the oil of vitriol. That part of the watery vapour which comes into contact with the oil of vitriol is absorbed, and a fresh evaporation takes place from A. The absorption of the vapour by B and its evolution from A go on at the same time and uninterruptedly, and the heat which the evaporating part of the water requires as latent heat is taken from the rest of the water. In this way the water in A may lose so much heat as to freeze.

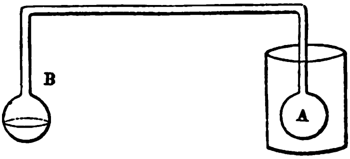
§ 114. Bodies which cannot be dried by heat on account of their being decomposed at high temperatures are frequently dried in this way under the receiver of the air-pump.

§ 115. The higher one ascends in the air the less is the pressure of the air, and the greater consequently the evaporation. Regions are habitable where the atmospheric pressure is so small that substances which are known under ordinary circumstances as liquids, such as ether, there exist naturally as gases, and can only be got in the liquid state by artificially increasing the pressure on them or taking the heat from them.

§ 116. Inversely, many bodies which are known under ordinary circumstances as gases may be converted into liquids, either by increasing the pressure upon them or by artificially cooling them. Thus the well-known gas carbonic acid becomes a liquid when it is either cooled to −78° C. at the ordinary pressure of the air, or compressed with a force of 28 atmospheres at the ordinary temperature. Ammonia becomes liquid when cooled to −33° C., or pressed with a force of 6 atmospheres, &c.

§ 117. The evaporation produced by diminished pressure and the cold produced by evaporation are both shown in the *Cryophorus* (fig. 30). It consists of two bulbs, A and B, joined together by a tube. When the instrument is made, a little water is put in. This is boiled; and when all the air is expelled, the tube

Fig. 30.



is sealed up. When the bulbs get cold the steam in them condenses, and, the air being excluded, there is present only vapour of water. If, now, the water is all made to flow into the one bulb, B, and the other, A, is surrounded by a freezing-mixture, the vapour in A condenses; and the pressure upon the water in B being removed, it gives off vapour to supply its place; the process is continuous until so much heat has left the water in B in order to become latent in the vapour which rises from it, that the remainder of the water in B freezes.

§ 118. When an evaporating liquid is placed in a confined space containing air or other gas, the evaporation will continue until the gas becomes saturated with the vapour. Since all gases and vapours mix with one another in all proportions, the quantity of the liquid evaporated in no manner depends upon the nature of the gas into which the evaporation takes place, but only upon its volume and the pressure and temperature common to both. A liquid evaporates as perfectly into any gas as it does into a vacuum; and although the rate is not so great in the former case, owing to the time required for diffusion, the final amount is the same.

§ 119. Hence if the atmosphere into which a liquid is evaporating be of indefinite extent, the whole of the liquid will ultimately evaporate; and this will take place the sooner the more rapidly the atmosphere is changed.

§ 120. The conversion of the liquid by evaporation into a gas is, of course, as before, accompanied by an absorption of heat by the vapour, and the production of sensible cold. The rapidity of evaporation and consequent amount of cold produced, depends upon the extent of the evaporating surface, and upon the rate at which the atmosphere is changed. The cold produced by evaporation into air is by far more common than that arising from evaporation into vacuum; and it is of great importance, because upon it depend the existence and distribution of water in the air and all the attendant phenomena.

§ 121. *Examples of cold produced by evaporation.*—When the body, through muscular exertion, mental excitement, or external heat, acquires a temperature likely to be prejudicial, the skin throws off moisture in the form of perspiration, which cools the skin by its evaporation. Water is cooled by exposing it in porous vessels to dry wind, by wrapping the water vessels in damp cloths, by exposing shallow lakes of water to the wind, &c. While in a bath, the body does not feel so cold as on leaving it, especially if there be a wind. Mercury may be frozen if brought into contact with strong ammonia, through which air is made to bubble rapidly. The greatest artificial cold is produced by the evaporation of a liquid which has been previously condensed from the state of vapour and cooled.

§ 122. It of course follows that when a vapour is forcibly compressed so as to become a liquid, in doing so it gives out its latent heat.

§ 123. Further, and inversely, a vapour dissolved in another vapour or gas may be condensed and withdrawn when the two are cooled. Hence if a cold body is brought into a room of a warm moist atmosphere, the air which is cooled by contact with the cold body, not being able when cold to hold so much watery vapour in solution, deposits it on the cold body as a sort of dew. In a crowded room or carriage, in cold weather, the glass of the windows is kept cold by the cold air outside; the inside surface becomes cooled and condenses the water which the warm air of the chamber has absorbed from the breath and perspiration of the people. The water in the breath may be generally condensed by breathing upon bodies of the ordinary temperatures. In cold moist weather the moisture of breath is given up in the form of mist as the breath becomes cooled.

§ 124. At night the earth no longer receives heat from the sun but gives off what it has received during the day. Its surface becomes cooled; the water in the air in contact with the earth condenses upon the earth as *dew*. If the weather be very cold, the dew as formed freezes and is called *hoar-frost*.

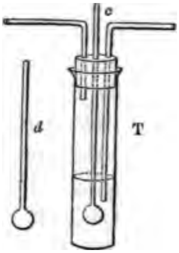
§ 125. *Fog, mist, cloud, rain, hail, snow*.—When a mass of the atmosphere saturated (or nearly so) with watery vapour becomes cooled, the water separates in the liquid state from the air in little spherical globules, which are often so small that they do not sink rapidly to the earth. Such is called *fog* or *mist* when we are amongst it, *cloud* when seen from a distance. The upper parts of the air being cooler than the lower ones, it frequently happens that when a quantity of air is forced to rise, it becomes so cooled as to give up its water as mist. Hence the tops of mountains are frequently covered with clouds, because the warm moist wind moving along the earth is turned upwards by the mountain-side into a region where, being cooled, it can no longer hold so much water in solution.

§ 126. When the little globules of mist get so numerous, or grow so as to fall rapidly, *rain* is produced. If the mist be frozen before it collects into drops, it falls as *snow*. If it be frozen after it has collected into rain-drops, it falls as *hail*.

§ 127. The quantity of moisture in the air is most exactly determined by passing a known volume of the air through some substance eager to absorb water, such as oil of vitriol. The increase in weight of the substance is of course the moisture in the air. The determination of the quantity of moisture in the air is called *hygrometry*, and the instruments used for the purpose are *hygrometers*.

§ 128. It is clear, from what has been stated, that if there be a great quantity of vapour in the air (that is, if the air be nearly saturated with water), a very small depression of temperature will cause a separation of the vapour as dew upon the body which is used to cool the air. And, conversely, the extent to which the temperature must be depressed in order to produce dew is a measure of the quantity of moisture in the air. The dew-point hygrometer (fig. 31) is a little tube, T, of black glass or bright metal,

Fig. 31.



containing some ether. Three holes are bored in its cork; through one passes the tube *a*, which reaches nearly to the bottom of T; through the other passes a short tube, *b*, and through the third passes a thermometer, *c*. Another thermometer, *d*, shows the temperature of the air. Air is forced through *a* or drawn through *b*; in both cases it bubbles through the ether in T and evaporates it, thereby depressing its temperature, and consequently that of the tube T; after some time the surface of T is seen to become dull, owing to the condensation on its surface of the water of the air. The temperature of the ether is then read on the thermometer *c*, and that of the air on the thermometer *d*. The difference measures the degree of moisture in the air—the greater the difference the less being the moisture, or the dryer the air.

CHAPTER XII.

Ebullition.

§ 129. The tension of the vapour of a liquid increases with the temperature. If the temperature be so raised that the vapour-tension is exactly equal to the pressure of the air, the two are in unstable equilibrium, and the slightest increase of temperature will cause the liquid to *boil*. Bubbles of vapour are formed in the liquid; these rise and break on the surface, whence they spread through the air. The temperature at which this ebullition or boiling takes place is called the "boiling-point" of the liquid.

§ 130. The boiling-point of a liquid is of course found by examining a thermometer whose bulb is either in the liquid as it boils, or in the vapour thence arising.

§ 131. The boiling-points of different liquids under the same circumstances are very different. The following list shows the temperature at which a few liquids boil under the ordinary pressure of the air (760 millims.).

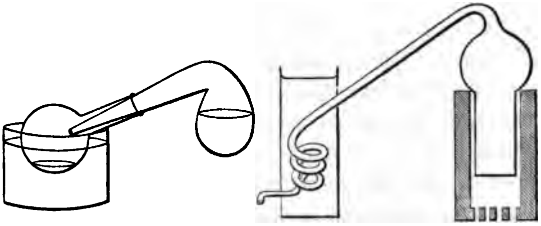
Ammonia	−33° C.
Ether	+34
Alcohol	78
Water	100
Phosphorus	290
Mercury	360
Zinc	1040

§ 132. The boiling-point of a liquid varies slightly with the nature of the surface of the vessel which contains it. Liquids boil at the lowest temperatures (and such are regarded as their true boiling-points) in metallic vessels and such as have rough surfaces. In very smooth glass vessels the liquid frequently rises in temperature a few degrees above its true boiling-point; then takes place a sudden burst of vapour, which carries off the extra heat as latent heat, the residual liquid sinking in temperature.

§ 133. Difference of boiling-point often offers a convenient means for the separation of liquids from a mixture. The manufacture of rum, whisky, or spirits of wine from fermented liquids depends upon the fact that alcohol boils at a lower temperature than water, and that, if a mixture of the two be heated to a temperature between the boiling-points of the two (78° C. and 100° C.), most of the alcohol is distilled off and most of the water remains behind.

§ 134. The vapour of a boiling liquid is generally condensed by being made to pass into a vessel externally cooled by water (fig. 32).

Fig. 32.



§ 135. When the pressure upon a liquid is increased, the temperature at which it boils is raised. The heat must be greater before the tension of the vapour overcomes the increased pressure. On the tops of mountains the pressure of the air is less, because there is a less quantity of air above, and that of a less density. Hence in high regions water boils below 100° C. At the bottom of mines it boils above 100° C. By determining the temperature at which water boils, we may therefore get a measure of the height of a mountain.

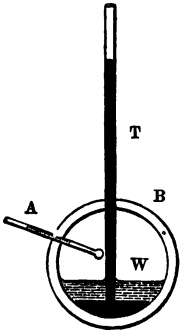
§ 136. Also, if the pressure of the air be lessened artificially by its total or partial removal, the boiling-points of liquids at the surface of the earth are lowered.

Use is made of this in the arts—as, for instance, in evaporating the water from cane-juice or in sugar-refining. If the saccharine liquid be boiled and concentrated under the ordinary atmospheric pressure, the heat necessary to boil it is so great as to blacken the sugar; but by boiling it *in vacuo* the boiling-point is lowered, and the syrup may be so concentrated, without injury to its colour, that it crystallizes on cooling.

§ 137. If a flask of water be boiled briskly (so as to be full of only water and steam) and then corked, removed from the flame and inverted, the water may be made to boil long after its temperature has fallen below 100° C., by pouring cold water on the upper part; for on doing so the steam is condensed, and, a partial vacuum being formed, the water boils at a lower temperature.

§ 138. The relation between the boiling-point and pressure is seen on heating a quantity of water, W (fig. 33), in a boiler, B, through the top of which passes, steam-tight, a tube, T, open at both ends and dipping below into some mercury beneath the water. A thermometer, A, also passes through the side of the boiler. When the boiler is heated the steam presses upon the surface of the water and forces the mercury up the tube T. The

Fig. 33.



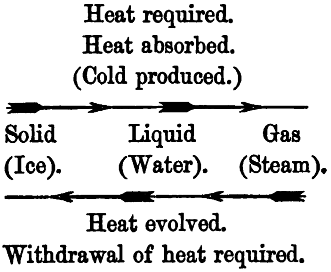
higher the temperature, as shown by A, the greater the pressure, as shown by the level of the mercury in T. The following Table shows the temperatures at which water boils when subjected to the pressure of more than one atmosphere:—

Pressure, in atmospheres.	Boiling-point. C.
1	100
2	121
10	181·6
20	214·4
50	266

The *pressure* of steam in a boiler may thus be known by finding the *temperature* of the steam.

§ 139. The boiling-point of a liquid is also altered by dissolving in it solids or other liquids. The dissolved body, if it be a solid, appears to adhere to the liquid and keep back the vapour, necessitating the application of a greater heat. Thus a saturated solution of common salt boils at 108°·3 C.

§ 140. The following diagram illustrates, and may serve as a means of recalling, the relation of heat to the three forms of matter.



Heat required.
Heat absorbed.
(Cold produced.)

Solid (Ice). Liquid (Water). Gas (Steam).

Heat evolved.
Withdrawal of heat required.

CHAPTER XIII.

CONDUCTION OF HEAT.

§ 141. When one part of a body receives a certain addition to its temperature, the heat travels through the mass of the body in all directions, until the entire body attains a higher temperature. If, for instance, we suppose a mass of iron of 100 cubic inches to have the uniform temperature of 0° C., then, if one of those cubic inches be suddenly heated to 100° C., it will heat the remaining 99 cubic inches to 1° C., itself falling in temperature to 1° C., so that the result will be 100 cubic inches at 1° C.

§ 142. The passage of heat through the mass of the substance, without any sensible motion taking place in the matter itself, is called the *conduction* of heat; and the substance through which the heat travels is called a *conductor.*

§ 143. Further, if any part of a body receives a continual supply of heat by being constantly maintained at the same elevated temperature (as by plunging the part into boiling water), the whole of the body will gradually acquire the same temperature by conduction.

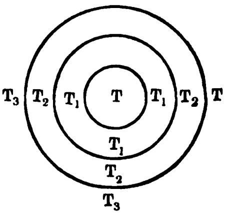
§ 144. Inversely, if the temperature of one part of a body is reduced, the heat from the warmer is conducted into the cooler part until the whole body has a uniform temperature. Thus, if a mass of iron of 100 cubic inches volume have the temperature 100° C., and if one of those cubic inches be cooled to 0° C., the heat will pass into the cool cubic inch until its temperature reaches 99° C. The remaining 99 cubic inches having each thereby lost 1° C., they also will have the temperature 99° C., so that the entire mass will have the temperature of 99° C.

§ 145. Again, if heat be continually withdrawn from a part of a body (as by plunging that part into melting ice), heat will travel through the rest of the body towards the cooler part, until the whole body attains the temperature of the cooler part.

§ 146. Conduction of heat through a body is a particular instance of the general law, that when two bodies of different temperature are in contact, the hotter will give heat to the cooler until the temperature of the two are equalized. In the condition of bodies of unequal temperature are the unequally heated parts of the same material mass.

§ 147. All substances without structure (that is, all gases, all liquids, and all such solids as have no crystalline form*) conduct heat equally in all directions; so that, if there be no motion of the parts of the body, and a point in the interior of the mass of such a body be heated, at any given time the temperatures at different points on the surface of any sphere whose centre is the heated point T, are the same (fig. 34). But the temperature of the various spherical shells $T,_1$ T_2, T_3, &c. are different.

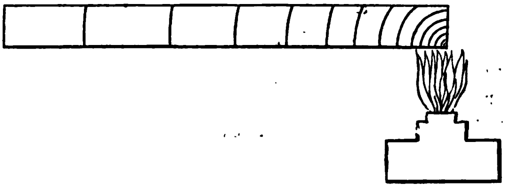
Fig. 34.



§ 148. If one end of a solid bar be continually heated, at the same instant of time the different parts of the bar at different distances from the source of heat will be of different temperatures (fig. 35).

§ 149. If there were no loss of heat (by radiation and convection by the surrounding air) the whole bar would at last acquire the same temperature as the heating influence. This is really never the case; one end of a long metallic bar may be kept at a red heat for any length of time while the other is held in the

Fig. 35.



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* Masses of wood, ivory, &c. of course conduct heat with different power according to the relative positions of the path of the heat and the direction of the fibres or layers of the organized body. In the above paragraph it is supposed that the body has the same composition throughout.

hand, because the heat in travelling along the bar escapes, partly by radiation (see §§ 169 & 170), and partly by the convection of the air (see § 163).

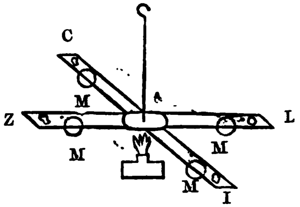
§ 150. Solids conduct heat better (more quickly) than liquids, and liquids better than gases.

§ 151. Of solids, the metals, as a class, conduct heat the best.

§ 152. The relative conducting-power of solids for heat may be determined by heating to the same temperature the ends of similar rods of them, and measuring either the time which it takes for the other ends of the rods to acquire any the same temperature, or by comparing the temperatures of the ends of the rods after a given time.

Thus (fig. 36) if four equal and in every way similar rods of copper, iron, zinc and lead, H C, H I, H Z, and H L, are fastened together and equally heated at H by the lamp F; and if marbles, M, M, M, M, are stuck with wax on the under sides of the four rods; or if fragments of phosphorus, P, are placed at equal distances from H upon them: then, on applying a flame at H, the marbles will be found to fall in the order C, I, Zn, L. The phosphorus will also be ignited in the same order. Hence copper is a better conductor than iron, iron than zinc, and zinc than lead.

Fig. 36.



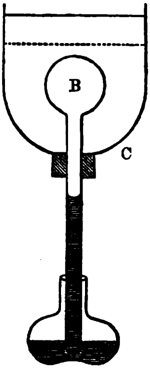
§ 153. The following Table shows the conducting-powers of a few metals:—

Metal.	Conducting-power.
Silver	1000
Copper	736
Gold	532
Tin	145
Iron	119
Steel	116
Lead	85
Platinum	84
Bismuth	18

From this it is seen that the conducting-power by no means follows the same order as the expansion (§ 35), or as the specific heat (§ 83), or as the density.

§ 154. *Conduction of heat by liquids.*—The conducting-power of liquids is exceedingly small, and owing to the motion generally caused by change of density when a part of a liquid is heated, the conducting-power is difficult to measure. The following experiment shows how small is the conducting-power of water. The bulb of an air-thermometer (fig. 4, § 20) is enclosed in a cup C (fig. 37), which is then filled with cold water until the bulb B is covered. Hot water is then poured upon the surface of the cold water in such a way as not to disturb the latter. The hot water being the lighter, rests upon the surface of the cold. It is found that the air in the bulb B remains for a long time at its original volume, showing that the heat has not been conducted downwards. The glass of the cup C, however, conducts a portion of the heat of the hot water downwards, and this causes motion to take place in the colder water, so that at last the bulb becomes warm.

Fig. 37.



The author has recently shown that, of about twenty liquids examined, mercury conducts the best and water the next, and that all liquids conduct heat sensibly.

The conduction of heat by gases is even less than that by liquids, and is indeed so small that it cannot be measured.

§ 155. The sensation of temperature depends in a great degree upon the conducting-power of the bodies with which the human body is in contact. If a piece of iron and a piece of wood be both heated to the boiling-point of water, the iron cannot be held in the hand without pain and injury, while the wood can be held with impunity; for the heat withdrawn by the fingers from the part of the iron in contact with them, is quickly replaced by fresh heat conducted through the iron. Such is not the case with the bad conductor wood; so that with wood the point held soon acquires the temperature of the fingers, and no heat is felt.

§ 156. The inverse is the case if both iron and wood are exceedingly cold. The iron withdraws the heat more rapidly and *feels* colder.

§ 157. The bad conducting-power of air is employed to keep uniform the temperature of rooms, by the application of double windows and doors. The enclosed air does not allow the heat to pass through,

§ 158. Solids mixed with gases, as hair, wool, cotton, &c., owe their bad conducting-power to the air which is entangled in them. Hence their employment as garments to protect the body from sudden changes of temperature.

§ 159. Even snow, owing to the air which is in it, is a very bad conductor of heat. Hence, sometimes, it is used for building huts; and it serves in nature to retain in winter the internal warmth of the earth, and to prevent the ground from being frozen deeply.

§ 160. If the air be still, the human body may be exposed with impunity to a temperature of from +50° C. to —50° C., because the air refuses to conduct the heat to or from it.

§ 161. If the hand and arm be moistened with water or a more volatile liquid, such as ether, it may be plunged without injury into melted iron. The vapour which the heat causes prevents direct contact between the metal and the skin, and refuses to conduct the heat from the former to the latter, &c.

§ 162. Those crystals which expand unequally in different directions when heated (§ 42), also conduct heat in the same directions with different rapidity.

CHAPTER XIV.

CONVECTION OF HEAT.

§ 163. It is clear that when a mass of matter of any temperature changes its place, the heat which is in it also moves with the body.

In such a case, the body is said to *convey* the heat. We have already had instances of the convection of heat when speaking of the motions caused by heat in the air and in the sea (§§ 23–33).

§ 164. Heat may be conveyed by either of the three forms of matter. Immense quantities of heat are conveyed through space by the movements of the earth and of the celestial bodies. But on the earth itself, convection is more common in fluids (gases or liquids), in consequence of the motion produced by change of density which always accompanies change of temperature, and because the parts of fluids move without difficulty among one another.

§ 165. Although liquids conduct heat very badly and gases perhaps not at all, yet a whole mass of either liquid or gas may be heated if heat be applied to only one point. Thus if, instead of applying heat to the surface of a vessel of water, the heat be applied below, as is generally the case, the hot water being lighter, rises. The cold water supplies its place and, reaching the source of heat, is heated in its turn (fig. 38). The hot water,

Fig. 38.

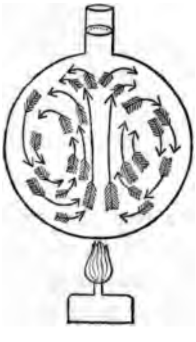
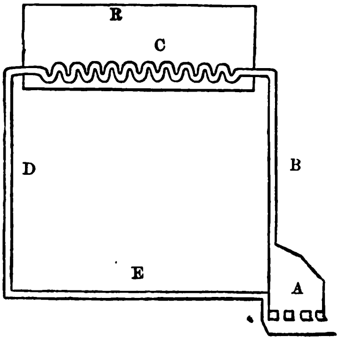


Fig. 39.



in rising through the cold, mixes with it and gives up some of its heat; so that at any time the whole water is of nearly the same temperature throughout, and rises gradually and uniformly to the temperature which the source of heat is capable of imparting.

§ 166. Precisely the same takes place on heating a mass of air.

§ 167. In cold climates, the rooms of large public buildings are frequently heated at a distance from the fire, by causing hot water, steam, or hot air to circulate in tubes through the rooms which are to be heated.

Thus (fig. 39) if air be heated in the chamber A, it will rise through the pipe B, and, on traversing the tube C, will give out its heat to the room R; becoming thereby cooled, it will sink through the tube D, and will pass through E to be again heated in A.

§ 168. Precisely the same effect is produced if water instead of air be heated in A. If the water in A be boiled the steam is condensed in C, gives out its latent heat and flows, as water, back again to the boiler A to be again heated, converted into steam, and put into circulation. Steam is more frequently used than hot water or air, because its temperature is more uniform and all danger of overheating is avoided.

Very important natural instances of the convection of heat have been already discussed in speaking of the effects of expansion (§§ 23–33).

CHAPTER XV.

RADIATION OF HEAT.

§ 169. It is generally supposed that whatever the actual temperature of a body may be, and whatever its temperature relatively to surrounding objects, it continually throws off heat in all directions. So that if two bodies of different temperatures are in the neighbourhood of one another, each one both gives heat to, and receives heat from, the other; but the quantity of heat given by the warmer to the cooler being greater than the quantity given from the cooler to the warmer, the cooler becomes warmed and the warmer cooled.

It amounts, however, in effect to very much the same if we suppose the hotter body only to lose, and the cooler body only to gain heat.

§ 170. When a body has a higher temperature than the surrounding bodies it gives them heat, even if it is not in contact with them, and even if it is out of contact with matter of any kind. And if a body be surrounded only (as far as is possible) by empty space of a lower temperature, it will throw off its heat, becoming at last as cool as the space in which it is placed. Finally, heat which is thrown off from a body not in contact with others may pass through certain material media without increasing their temperature. Heat travelling in any of these ways is called *Radiant heat.*

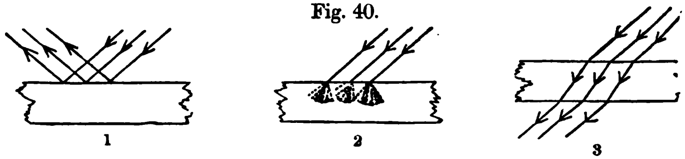
§ 171. The great source of radiant heat for the earth is the sun. The sun is hotter than the surrounding space; it gives off heat in all directions. This heat traverses celestial space; a part of it reaches the atmosphere of the earth. Some of it is employed in heating the air and the watery vapour in the air; a large quantity passes through the air and falls upon the sea and land. It penetrates but a little way into either, but expends itself in increasing their temperature and volumes, or changing their physical states.

§ 172. The radiant heat of the sun travels in straight lines, and, as far as is known, with the same velocity as light, that is, about 200,000 miles *per* second.

When radiant heat falls upon a substance three things may happen to it. (1) It may be *reflected*; the body does not get warm but the heat is thrown off again, undiminished in quantity but altered in direction. (2) It may enter the body and warm it, being *absorbed* by the body. (3) It may be *transmitted*, or pass through the body without sensibly warming it.

§ 173. In no case, however, does any one of these things take place alone. If they did so we might represent (fig. 40) a perfect reflector by (1), a perfect absorber by (2), a perfect transmitter by (3).

Fig. 40.



§ 174. But in all actual cases, a part of the heat is reflected, a part absorbed, and a part transmitted (fig. 41). Different bodies, however, have different reflective, transmissive, and absorptive powers; so that, in some cases, nearly all the heat is reflected, in others nearly all is absorbed, in others nearly all is transmitted.

Fig. 41.

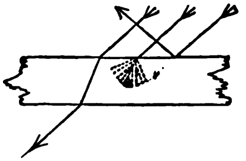
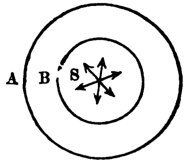


Fig. 42.



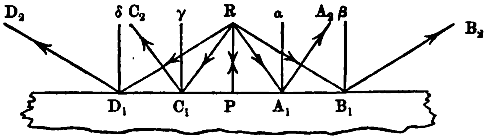
§ 175. If the heat which leaves a body as radiant heat suffers no diminution in entire quantity during its motion, it diminishes in intensity according to the square of its distance from the source of heat. For since (fig. 42) the entire heat given off in a given time from a hot body, S, is the same, there must fall the same quantity of heat on the spherical surface, A, as would have fallen upon the lesser spherical surface, B. The intensity of the heat on A must be less than that on B, according as the surface of A is greater than the surface B. Now the surfaces of two spheres are in the proportion of the squares of their radii. Therefore the intensity of the heat on A is to the intensity of the heat on B inversely as the square of S A is to the square of S B; and universally—

$$\frac{\text{Intensity at distance } D_1}{\text{Intensity at distance } D_2}=\frac{D_2^2}{D_1^2}.$$

§ 176. If radiant heat falls upon a perfect reflector, its direction is altered in exactly the same manner as is that of light and of sound; namely, the reflected heat makes the same angle with the surface, or perpendicular to the surface, as does the incident heat; and the incident heat, the perpendicular to the surface, and the reflected heat are in one plane.

Thus (fig. 43) if R be a body radiating heat in all directions, the heat $R A_1$ will be reflected in the direction $A_1 A_2$, so that if $A_1 \alpha$ be drawn from A_1 perpendicular to the surface, angle $R A_1 \alpha$ $=$angle $\alpha A_1 A_2$, and so on. Heat which falls perpendicularly to the surface as R P, will accordingly be reflected back again to the source of heat, R.

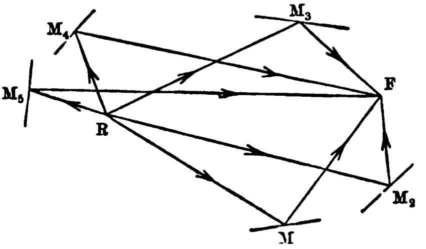
Fig. 43.



§ 177. If the source of heat be (like the sun) at a very great distance, all the heat which reaches us must have travelled nearly in the same direction; that is, such heat may be supposed to consist of parallel rays. In this case it is clear that the reflected rays must also be parallel, if the reflecting surface be a plane.

§ 178. It is possible so to arrange a number of small reflecting surfaces, that the heat which falls upon each of them may, after reflection, pass through one and the same point. Thus (fig. 44),

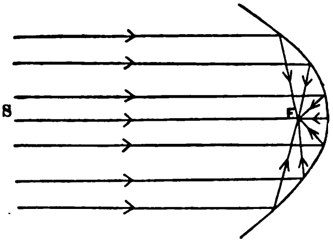
Fig. 44.



let R be a source of heat, and M_1 a reflecting surface; then the heat which falls in the direction RM_1 will be reflected in the direction M_1F; again, M_2 may be so adjusted that the incident ray, RM_2, may be reflected in the direction M_2F, and so on. The point F, to which all the reflected rays of heat converge, is called the focus. It is clear that if F be the source of heat, the reflectors M_1, M_2, &c. being in the same places, then the rays which leave F will, after reflection at the surfaces, converge to R, which will therefore be the focus. It is a general law that if the focus be made the source of heat, the original source of heat becomes the focus.

§ 179. If the parallel rays of the sun be allowed to fall upon a concave metallic reflector of the shape shown in fig. 45 (a parabola*), all the rays will be reflected to F, and a great heat produced there. Inversely, if a hot body be placed at F, the heat will travel in exactly the opposite direction; that is, from F they will diverge, strike upon the reflector, and thence be reflected parallely towards S.

Fig. 45.



§ 180. By combining two such reflectors the heat radiated from a body in one part of a room may be collected at another (fig. 46). If a red-hot iron ball be placed at B, the heat which is radiated strikes the first reflector, is thence thrown parallel to the central axes of both, strikes the second reflector, and is concentrated at A, its focus. There it may ignite gunpowder, or affect a thermometer, &c.

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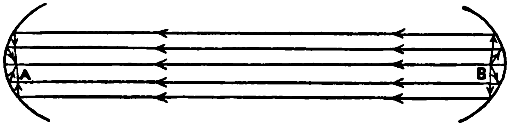
* The parabola has the property that if, from any point P of it, two straight lines be drawn, one to a certain point F, and the other parallel to the central line A F, then these two straight lines make equal angles with the tangent at the point P, or with a perpendicular to it.

Fig. 46.



§ 181. The same quality of surface which enables a body to oppose the entrance of heat, causing it thereby to be a good reflector, also resists the exit of heat from the body, and causes it to be a bad radiator. Metals are the best reflectors of heat, and the worst radiators. Smooth bodies are better reflectors and worse radiators than rough ones. Light-coloured bodies are better reflectors and worse radiators than dark-coloured ones.

§ 182. Again, the quality of surface which allows heat freely to escape, causing the body to be a good radiator, also allows the heat freely to enter; so that a good radiator is a good absorber of heat.

§ 183. The quantity of radiant heat which passes through a medium depends, 1st, upon the nature of the body from which the heat radiates, and 2nd, upon the nature of the medium. The power of allowing radiant heat to pass through is called *diathmacy.*

§ 184. The following list shows the percentage of incident heat from different sources which different solids allow to pass through; all the solids being about 0·1 inch in thickness.

	Heat of Oil-lamp.	Red-hot Platinum.	Copper at 390° C.	Copper at 100° C.
Rock-salt	92	92	92	92
Carbonate of lime ..	39	28	6	0
Plate glass	39	24	6	0
Alum	9	2	0	0
Sugar-candy	8	0	0	0
Ice	6	0	0	0

§ 185. Gases also possess different powers of transmitting heat. The following Table shows the comparative *absorbent power* of a few gases for heat radiated by copper at 270° C. The gases are all under the ordinary atmospheric pressure.

Atmospheric air	1	Carbonic acid	90
Oxygen	1	Nitrous oxide	355
Nitrogen	1	Marsh-gas	403
Hydrogen	1	Olefiant gas	970
Chlorine	39	Ammonia	1195

The further discussion of this point, and the consideration of the refraction or breaking of heat, would be out of the purpose of this elementary treatise.

PART II.

◆

CHEMISTRY OF THE MORE IMPORTANT NON-METALLIC ELEMENTS.

CHAPTER I.

General Notions.

§ 1. *Elements.*—Every substance, whether solid, liquid, or gaseous, consists of one or more substances which are called *elements*. The number of elements at present known is 64. Some of these elements are gases, some liquids; but the greater number are, under ordinary conditions, solid bodies.

§ 2. If a quantity of matter, such as a lump of sugar, be mechanically broken up or pounded, the small fragments are found to have precisely the same properties as the original mass. They have the same taste, the same colour, the same density, the same degree of solubility in water, and the same crystalline form as the original sugar. But if the sugar be strongly heated, it gives off various vapours and gases, and leaves as a residue a black substance called charcoal or carbon. This carbon may be heated and acted upon by any physical force in any manner, and, if it be alone, that is, excluded from contact with matter of a different kind, it will remain unaltered. By no means can it be changed in a way at all like the change suffered by the sugar. Carbon is called therefore an element of the sugar, or simply an element.

§ 3. In like manner it may be shown that two gases, which we shall learn to know as hydrogen and oxygen, may be got out of the sugar, and that they also, when separated, are quite unalterable. Further, it is found that if a given weight of sugar be taken and the quantities of hydrogen, oxygen, and carbon which can be got from it be weighed, the sum of the weights of the three elements is exactly equal to that of the original sugar. Hence it follows that only these three elements exist in sugar, or that sugar is made of the elements carbon, oxygen, and hydrogen.

§ 4. Any matter is therefore said to be in an elementary state, or to be an element, which resists all attempts to extract from it (or *decompose* it into) substances different from one another or from the original matter.

§ 5. All known natural substances have been examined with the endeavour to separate from them the elements which they might contain or consist of; in other words, attempts have been made to decompose them. Some natural substances have resisted all attempts to effect their decomposition; others, like sugar, have yielded and been broken up or decomposed into constituents, which, like carbon, hydrogen, and oxygen, resist further decomposition. In this way the 64 elements have been gradually found in nature or artificially obtained from natural compound bodies.

§ 6. The following Table contains the names of all the elements at present known. The meaning of the symbols (such as Al) and the numbers attached will be explained hereafter.

It will be seen at a glance that a good many of the elements which are metals occur in nature in the elementary state, although even these are most frequently impure.

Table of the Elements, with their Symbols and Combining Weights.

Element.	Symbol.	Combining Weight.	Element.	Symbol.	Combining Weight.
Aluminium	Al	27·4	Cadmium	Cd	112·0
Antimony	Sb	122·0	Cæsium	Cs	133·0
Arsenic	As	75·0	Calcium	Ca	40·0
Barium	Ba	137·0	Carbon	C	12·0
Bismuth	Bi	210·0	Cerium	Ce	92·0
Boron	B	11·0	Chlorine	Cl	35·5
Bromine	Br	80·0	Chromium	Cr	52·5

Element.	Symbol.	Combining Weight.
Cobalt	Co	58·7
Copper	Cu	63·5
Didymium	D	96·0
Erbium	E	?
Fluorine	Fl	19·0
Glucinum	Gl	9·3
Gold	Au	197·0
Hydrogen	H	1·0
Indium	In	74·0
Iodine	I	127·0
Iridium	Ir	198·0
Iron	Fe	56·0
Lanthanum	La	92·0
Lead	Pb	207·0
Lithium	Li	7·0
Magnesium	Mg	24·0
Manganese	Mn	55·0
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Nickel	Ni	58·7
Niobium	Nb	94·0
Nitrogen	N	14·0
Osmium	Os	199·2
Oxygen	O	16·0
Palladium	Pd	106·6
Phosphorus	P	31·0
Platinum	Pt	197·5
Potassium	K	39·1
Rhodium	Rh	104·4
Rubidium	Rb	85·4
Ruthenium	Ru	104·4
Selenium	Se	79·5
Silicon	Si	28·0
Silver	Ag	108·0
Sodium	Na	23·0
Strontium	Sr	87·5
Sulphur	S	32·0
Tantalum	Ta	172·0
Tellurium	Te	129·0
Thallium	Tl	204·0
Thorium	Th	115·7
Tin	Sn	118·0
Titanium	Ti	50·0
Tungsten	W	184·0
Uranium	U	120·0
Vanadium	V	137·0
Yttrium	Y	?
Zinc	Zn	65·2
Zirconium	Zr	89·6

§ 7. Inversely, it of course follows that all known bodies either consist of a single element or are composed of two or more elements.

§ 8. It is also self-evident that an element is the same, from whatever source it may be procured; otherwise, having different properties in the two cases, it would be entitled to be considered a different element and to bear a distinct name.

§ 9. Attempts have been and are continually being made to construct natural bodies out of the elements of which their decomposition has shown them to consist, and also to construct bodies unknown in nature by the artificial union of their elements. Great numbers of natural substances have thus been imitated, or rather artificially reproduced (for the artificially formed substance can in nowise be distinguished from the natural one); and immense numbers of substances unknown in nature are being yearly discovered.

§ 10. Since the elements separated from a compound body on its decomposition differ from one another and from the original substance, it follows that when elements are made to reunite so as to form the original body, they, in doing so, must lose their characters in such a way that the resulting body differs from them all. Such union is called chemical union or chemical combination.

Difference between Chemical Union and Mechanical Mixture.

§ 11. Two solid substances, such as sand and sugar, may be mixed mechanically to any degree of intimacy. But

(*a*) By careful examination the particles of sand may be distinguished lying amongst those of the sugar;

(*b*) The colour, taste, density, &c. of the mixture are intermediate between those of the sugar and sand; and

(*c*) The sugar may be completely separated from the sand by dissolving the former out with water.

Again, the two substances water and salt may be mixed, the salt being dissolved in the water. Then

(*d*) No examination can show the particles of salt separate from those of the water. But

(*e*) The taste, density, &c. of the mixture is intermediate between those of the salt and of the water; and

(*f*) The salt can be entirely freed from the water by boiling the latter away.

Finally, alcohol and oil of turpentine may be mixed. Then

(*g*) The taste, density, &c. of the mixture are between those of its constituents; and

(*h*) The alcohol can be separated from the oil of turpentine by the addition of water.

§ 12. The sugar and sand, the salt and water, and the alcohol and oil of turpentine are said in such cases to be mechanically or, more properly, physically mixed with one another. The marks of physical mixture are then, briefly, the intermediate nature of the compound between those of its constituents, and the facility with which it may be separated into them*.

§ 13. Further, when bodies are simply physically mixed, there is either no change of temperature at all, or generally an absorption of heat (§§ 98, 99, I.).

§ 14. If mixture takes place at all between two bodies, it may take place in an infinite number of proportions, though not necessarily in all proportions. Thus sand and sugar may be pounded together in all proportions. Alcohol and oil of turpentine may be mixed in all proportions. Salt and water may be mixed in an infinite number of proportions, from the weakest to the strongest brine; but not in all proportions.

§ 15. Elements or compound bodies, when in contact with one another, undergo under some circumstances a very much greater change than that brought about by their physical mixture. Thus, if the solid element carbon be heated in contact with the gaseous element oxygen, or in common air (which contains oxygen), the carbon gradually disappears, and a gas is formed resembling air—that is, colourless and transparent, having no smell, and only a feeble taste. The wasting away of the carbon is known in common language as its burning or combustion. It is accompanied by the liberation of heat and of light. Not only are the constituent elements, carbon and oxygen, of the new substance so intimately blended as not to be distinguishable from one another, but they cannot be separated by any physical means. The new gas has some resemblance to oxygen; but it instantly suffocates animals immersed in it, and extinguishes burning bodies. It has no resemblance whatever to carbon. This and similar changes are instances of *chemical union* between the elements concerned. The two elements are *united chemically*; *chemical synthesis* has been performed; a *chemical* compound has been produced.

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* If the bodies mixed are identical in nature, as when a pint of water is mixed with a quart of water, they cannot by any means be resolved into their original parts; nor could it be ascertained whether this had been effected or not.

§ 16. Similarly, if the two elements sulphur and iron be heated together, they get red-hot, shrink, and a black, porous body results, which resembles neither iron nor sulphur; for it has very few properties of either. It is a chemical compound of the two elements. It can only be melted at a high temperature, is destitute of the metallic lustre, is soft and friable, is scarcely at all attracted by the magnet, and resembles outwardly a black stone.

§ 17. Bearing in mind the difference in physical peculiarity which is almost always brought about by chemical union, there is little difficulty in admitting that the innumerable varieties of compound matter met with in nature are the result of the chemical union of two or more of the elements already enumerated (§ 6). That such is indeed the case is absolutely proved by the possibility of decomposing all known compound bodies into two or more of the elements already known.

§ 18. Further, if in the first instance of chemical union given (§ 15) the carbon is weighed before it is burnt, and if it is burnt in a great abundance of oxygen, then the weight of the new gas formed is exactly and invariably 3·66̇ times as much as the weight of the carbon burnt. But if the carbon be greatly in excess of the oxygen employed, the result will be a gas weighing only 2·33̇ times as heavy as the carbon consumed, and having very different properties from the gas got with excess of oxygen.

§ 19. Thus if 10 lbs. of carbon is burnt in both cases, the gas got in the first case will weigh 36·6̇ lbs., in the second only 23·3̇. Since what is not carbon in the gas is oxygen, it follows that the gases are composed as follows:—

I.		II.	
Carbon	10	Carbon	10
Oxygen	26·66̇	Oxygen	13·33̇
	36·66̇		23·33̇

That is to say, for the same quantity of carbon the second gas contains exactly half as much oxygen as the first. If, now, the second gas be heated with an excess of oxygen, it combines with again as much, and becomes converted into the first gas. And half the oxygen may be extracted from the first gas, whereby it is converted into the second. These two gases have very different properties, and may be easily separated from one another. If a quantity, say, 10 lbs. of carbon, be heated with more than $13\cdot\dot{3}$ and less than $26\cdot\dot{6}$ of oxygen, some of each kind of gas will be formed. But $\frac{10}{13\cdot\dot{3}}=\frac{12}{16}$, and $\frac{10}{26\cdot\dot{6}}=\frac{12}{32}$ exactly.

§ 20. Hence it appears that there are two chemical compounds possible between carbon and oxygen, different in nature according to the proportion between the two elements, and that if there be the same quantity of carbon, the oxygen of the one bears a very simple relation to the oxygen of the other; namely,—

A.		B.	
Carbon	12	Carbon	12
Oxygen......	32 (=2×16)	Oxygen......	16

§ 21. It is found that whenever oxygen and carbon unite chemically, whether alone or in presence of other elements, the proportion between the carbon and the oxygen is *invariably that of* 12, *or some multiple of* 12, *to* 16, *or some multiple of* 16.

§ 22. In the second instance of chemical union given (§ 16), according to the quantities of iron or of sulphur present, chemical compounds of iron with sulphur are formed, differing from one another, not of course in the nature of, but in the proportion between the elements. Thus the following bodies are known:—

(1)		(2)		(3)	
Iron	56	Iron	56	Iron	392 (=7×56).
Sulphur...	32	Sulphur ...	64 (=2×32)	Sulphur ...	256 (=8×32).

All these bodies contain the iron and sulphur in the proportion of 56 to 32, or some multiple of 56 to some multiple of 32.

§ 23. The main differences between a chemical compound and a mixture are then as follows:—

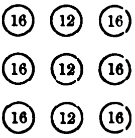
In a chemical compound.	*In a physical mixture.*
(*a*) The compound differs in physical properties from all its constituents.	(*a*) The mixture resembles one or other constituent according to their relative quantities.
(*b*) A compound generally cannot be easily decomposed or separated into its constituent elements.	(*b*) The mixture can generally be easily separated into its constituent elements.
(*c*) The union of elements chemically is attended by the liberation of heat.	(*c*) The physical mixture of bodies is not attended by the liberation of heat, unless change of state is produced (I. § 140). Often heat is absorbed, or cold produced.
(*d*) A single chemical compound always contains its constituents in certain fixed proportions by weight, or in multiples of those proportions.	(*d*) When two bodies mix at all, they may be made to do so in an infinite number of proportions.

CHAPTER II.

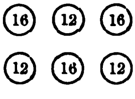
ATOMIC HYPOTHESIS. COMBINATION BY WEIGHT AND BY VOLUME. EQUIVALENTS.

§ 24. In order to explain the reason why elements should unite with one another only in definite proportions, recourse is had to an hypothesis or theory, called the Atomic Theory. It is supposed that every element consists of exceedingly small particles or atoms, of unknown shape, size, distance from one another, and absolute weight, but all in the same element precisely alike. Each of these atoms is indivisible and unalterable. In solids and liquids they are held together by a force called *cohesion*; in gases this force does not exist. Though the actual weight of a single atom of any one element is unknown, the *relative weights* of the atoms of two elements may be known, provided we know the *relative number* of atoms of the elements which unite to form a chemical compound, and the *weight* of the quantities of the two combined elements.

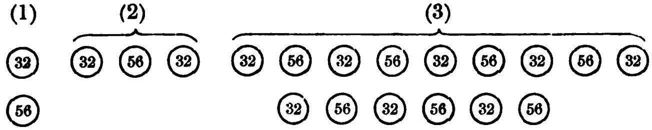
Thus (§ 20) if the one gas, A, resulting from the union of 12 parts by weight of carbon with 32 parts by weight of oxygen consist of twice as many atoms of oxygen as of carbon, it follows that the weight of an atom of carbon is to that of an atom of oxygen as 12 is to 16. The gas may be supposed to be represented as in the margin. The circles marked 12 represent the atoms of carbon, those marked 16 represent the atoms of oxygen. Whatever quantity of such a gas be taken, the relative quantity of the elements is clearly as 12 to 32.



In the gas B, which contains only half as much oxygen for the same weight of carbon as A, it is supposed that there are only half as many atoms of oxygen as in the first diagram. Here whatever quantity of gas is taken, the proportion between the elements is always as 12 to 16.



§ 25. Similarly, in the instance of sulphur and iron (§ 22), the first is supposed to contain equal numbers of atoms, so that the weight of an atom of iron is to the weight of an atom of sulphur as 56 is to 32. The second compound contains 2 atoms of sulphur to 1 of iron; the third contains 8 atoms of sulphur to 7 of iron.



The *atomic weight* of iron is said to be 56, that of carbon is 12, that of sulphur is 32, that of oxygen is 16.

It must be borne in mind that it is entirely a matter of guess and convenience when it is affirmed that the gas A contains two atoms of the one element to one atom of the other. There is no evidence whatever to prove that such is the case; and, indeed, in many similar cases the opinions of chemists differ.

§ 26. The simplest atomic relation in which two elements can combine is atom for atom. Thus the two gaseous elements, hydrogen and chlorine, unite with one another only in the proportion of 1 part by weight of hydrogen to 35·5 of chlorine. It is supposed that the atom of chlorine is 35·5 times as heavy as that of hydrogen, and that, when they unite, equal numbers of atoms combine.

§ 27. The cause of elements uniting chemically is referred to a force called *chemical affinity*, or simply *affinity*. Chemical affinity can of course only take effect between different matter in actual contact; and in the case of bodies which do not mix, it can only act at the points or surface of contact.

§ 28. When two bodies mix completely, as salt and water, the atoms of the bodies simply mutually interpenetrate, and in most cases the atoms of each body separate further from one another than they were before. When they unite chemically, there is an approaching of the atoms of the one body towards those of the other, although this does not necessarily make the volume of the compound less than that of the sum of the volu of the constituents. Thus, let there be two elements *a* and *b*. We may imagine their atoms, separate, mixed, and combined, to be respectively as follows:—

Separate Elements.		Mixed Elements.	Combined Elements.		
a a a	b b b	a b a b a b	ab	ab	ab
a a a	b b b	b a b a b a	ba	ba	ba
a a a	b b b	a b a b a b	ab	ab	ab

The approach of the atoms is accompanied by a liberation of heat; and the closeness of their union hides the properties which each has in the separate state.

§ 29. The function of elements in the material world may be aptly compared to that of letters in a language.

(*a*) There are 26 letters in the alphabet.	(*a*) There are 64 elements in nature.
(*b*) A letter may stand by itself and have a definite meaning.	(*b*) Each element may be alone and form a substance of definite property.
(*c*) No single letter can be divided so that its parts have any meaning.	(*c*) No element can be decomposed into separate elements.
(*d*) Letters and syllables may be joined together and produce no meaning.	(*d*) Elements and compounds may be mixed without producing any definite compound.
(*e*) Letters and syllables may be so arranged as to produce words having a distinct sense.	(*e*) Elements and compounds may be so united as to produce bodies having a definite nature.
(*f*) Words spelt nearly alike may have very different meaning.	(*f*) Compounds nearly the same in kind and quantity of their elements may differ very widely in properties.
&c.	&c.

§ 30. The theory of atoms is convenient, and its use often saves circumlocution; but it is to be remembered that there is no direct evidence of its truth beyond the convenience arising from its adoption.

§ 31. The fact, however, is thoroughly established that, whether owing to the existence of atoms or not, elements combine with one another in definite proportions by weight. These proportions are called the *Combining proportions* or combining weights of the elements. Thus, taking the elements already mentioned, sulphur, carbon, oxygen, and iron:—

12 parts by weight of carbon unite with 2 × 16 parts of oxygen,
32 „ „ sulphur „ 56 „ iron.

Further, it is found that

12 parts by weight of carbon unite with 2 × 32 parts of sulphur,
32 „ „ sulphur „ 2 × 16 „ oxygen.

If, therefore, the body consisting of 12 carbon and 2 × 16 oxygen be decomposed, and the resulting carbon be made to combine with sulphur, so that the new body consists of 12 carbon and 2 × 32 sulphur, the 2 × 16 oxygen have been replaced by 2 × 32 sulphur, or 16 oxygen by 32 sulphur; a body is thus got very similar to the original one. The 32 sulphur are said to *replace* the 16 oxygen, to play a similar part with regard to the carbon, to be *equivalent* to them.

Similarly, the compound 56 iron and 32 sulphur may have its 32 sulphur replaced by 16 oxygen. The 16 oxygen is equivalent to the 32 sulphur. Again, the body 12 carbon and 2 × 16 oxygen may have its 12 carbon replaced by 32 sulphur.

§ 32. Hence the numbers 32, 56, 16, 12 are called sometimes the *Equivalents* of sulphur, iron, oxygen, and carbon respectively; and such a body as sulphur 32 with oxygen 2 × 16 is said to contain two equivalents of oxygen, &c. It is therefore seen that the *Atomic weight*, the *Combining proportion by weight*, and the *Equivalent* of a body have nearly the same meaning. All three expressions are objectionable, being often limited in their meaning. We shall generally use the term equivalent—it being, however, always remembered that no quantity of one element can be in the fullest sense equivalent to a quantity of another element, because the substitution of one element for another in a compound always produces some change in the physical and chemical properties of the compound; no two bodies perfectly resemble one another which contain different elements. Thirty-two parts by weight of sulphur are chemically equivalent to sixteen of oxygen, in the same sense that a gold sovereign is commercially equivalent to twenty silver shillings; and as each of the sums of money may be exchanged without loss for one another or for one and the same quantity of goods, so may the thirty-two parts by weight of sulphur be exchanged for sixteen of oxygen, or either may be exchanged for twelve of carbon or fifty-six of iron.

§ 33. It is clear that the combining proportions, atomic weights, or equivalents have only a *relative* magnitude; that is, if 32 sulphur unites with 12 carbon to form a definite compound, then the same compound, though less of it, will be formed if 16 sulphur unites with 6 carbon, or if 8 sulphur unites with 3 carbon &c.

Just as in determining the specific gravities of bodies (see Natural Philosophy), or their specific heats (§ 78, I.), we took at will some convenient substance (water) as a standard of comparison and considered its specific gravity or specific heat as unity, so some element is selected whose equivalent is easily compared with those of other elements, and this equivalent is taken as unity.

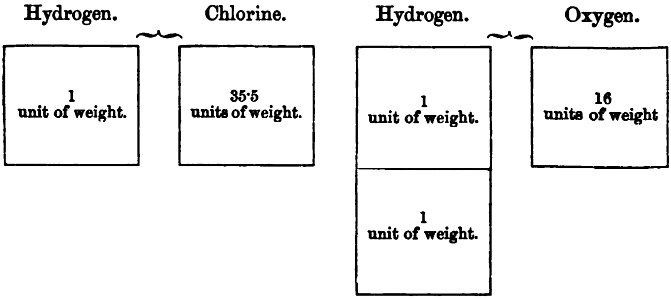
It is now almost universally agreed to take the equivalent of the element hydrogen as unity. The equivalent of hydrogen is less than that of any known element. If 1 lb. of hydrogen unites with chlorine, 35·5 lbs. of chlorine are required; if with oxygen, 8 lbs. are sufficient; if with sulphur, 16 lbs., and so on. The equivalents of oxygen, sulphur, and chlorine would therefore be 8, 16, and 35·5, if, the equivalent of hydrogen being 1, in all three cases the elements united atom for atom; but, for reasons which will be given, it is supposed that *two* atoms of hydrogen are concerned in all these cases, with the exception of chlorine. Hence the equivalents of oxygen and sulphur are 16 and 32 respectively, that of chlorine being 35·5. It is evident that if the equivalent of any other element were taken as unity, or indeed as any arbitrary number, the equivalents of all the elements would still bear the same *proportion* to one another, although expressed by different numbers. Sometimes the equivalent of oxygen is taken as 100. The resulting numbers for the equivalents of the other elements become then inconveniently large and difficult to remember. We shall take the equivalent of hydrogen as 1, and adopt the equivalent numbers given in § 6. II.

§ 34. *Combination by volume.*—It follows from Boyle's law and from § 18, I., that if any two gases or vapours have a definite relation to one another by volume at any one pressure and temperature, they will still bear the same proportion at every other pressure and temperature, provided, in the case of vapours, no liquefaction takes place.

§ 35. If such volumes of two gases are taken that, when mixed and united chemically, nothing of either is left, the original volumes are found to bear a very simple relation to one another. Or if a body which is a chemical compound of combined gases be decomposed, the volumes of gas of the different elements are related very simply to one another. Thus, in order that the two gaseous elements chlorine and hydrogen may unite completely, we must take exactly equal volumes of them; or if the compound of chlorine and hydrogen be decomposed, equal volumes of the gases are obtained; but the weight of chlorine required to combine with any quantity of hydrogen is 35·5 times as great as the weight of the hydrogen; hence the one volume of chlorine weighs 35·5 times as much as the one volume of hydrogen. The density of chlorine compared with hydrogen is 35·5, or is the same as the equivalent of chlorine.

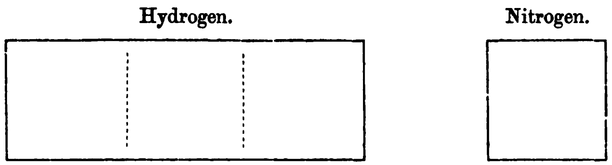
If equivalent weights of the two gases, hydrogen and oxygen, be taken—that is, if the weights of the two gases are in the proportion of 1 to 8 or 2 to 16, it is found that the volume of the hydrogen is exactly twice as great as that of the oxygen; in other words, the density of oxygen is exactly 16 times that of hydrogen. Inversely, if the compound of oxygen with hydrogen (which is water) be decomposed, for every cubic inch of oxygen obtained there will be two cubic inches of hydrogen.

The relation is shown in the following figure:—



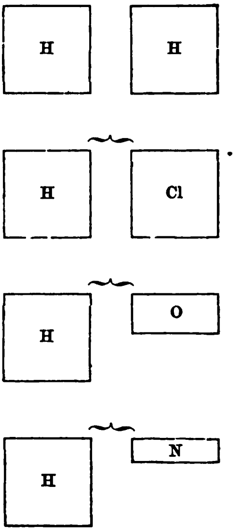
In all cases in which gaseous elements or compound gases unite, they are found to do so in very simple proportions with regard to volume, as in the above cases, as 1 to 1 or 1 to 2 (or 2 to 1). This is equivalent to the fact that there is always a simple numerical relation between the equivalent of a gaseous element and its specific gravity, referred to hydrogen as unity, or (recurring to the atomic theory) that in equal volumes of any two gases there are the same number of atoms of each element.

§ 36. Again, if the gaseous element nitrogen unites with hydrogen, it is found that exactly three volumes of hydrogen are required to unite with one volume of nitrogen.



Hence we have three distinct cases:—

1 volume of chlorine unites with 1 of hydrogen,
1 „ oxygen „ 2 „
1 „ nitrogen „ 3 „
or 1 volume of hydrogen unites with 1 of chlorine,
1 „ „ „ ½ of oxygen,
1 „ „ „ ⅓ of nitrogen.



Referring to the notion of equivalence, if two equal volumes of hydrogen be taken, half the hydrogen, or 1 vol., may be exchanged for and replaced by 1 vol. of chlorine or ½ vol. of oxygen or ⅓ vol. of nitrogen, as in figure. Or

The *equivalent volume* of hydrogen being taken as unity,

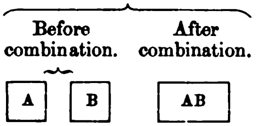
The equivalent volume of chlorine is 1,
„ „ oxygen is ½,
„ „ nitrogen is ⅓.

§ 37. When equal volumes of gaseous elements unite, the volume of the resulting vapour or gas is generally equal to the sum of the volumes of the separate gaseous elements.

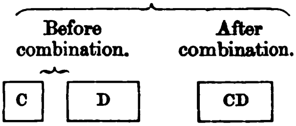
When one volume of one gas unites with two volumes of another, the gases on uniting usually contract to two volumes, or to the volume of the gas which had the greater volume.

When one volume of one element unites with three of another, the resulting compound has generally two volumes.

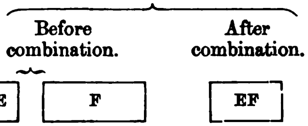
I.



II.



III.



§ 38. The specific gravity or density of compound gases, compared with hydrogen, may therefore be readily found if we know the volumes of the elements which combine and the contraction, if any, which they undergo in uniting.

Thus, in comparison with hydrogen, the density of the compound resulting from the union of equal volumes of hydrogen and chlorine, without contraction, is $\frac{35\cdot5+1}{2}=18\cdot25$. The density of the gas resulting from the union of two volumes of hydrogen with 1 volume of oxygen and contraction to two volumes is $\frac{2+16}{2}=9$. (This gas is the vapour of water.) The gas resulting from the union of three volumes of hydrogen with one volume of nitrogen and contraction to two volumes has the density $\frac{14+3}{2}=8\cdot5$.

§ 39. The specific gravity of gases is often referred to atmospheric air as unity. Air is 14·5 times as heavy as hydrogen. To get the specific gravity of a gas referred to air from that of it referred to hydrogen, we must therefore divide by 14·5. Referred to air, therefore, the first of the gases mentioned in § 38 has the density 1·260; the second has the density 0·621; the third has the density 0·586.

§ 40. No simple relation has been found between the volumes of liquid or solid elements which are necessary to combine with one another. The same solid element may frequently have different densities; that is, the same volume of it may contain various quantities of solid matter: further, the expansion of solid and liquid matter by heat is by no means regular, like that of gases (see Part I.); so that a volumetric relation at one temperature does not hold good at another.

§ 41. But elements which in the separate state are only known as solids or liquids, may exist in the gaseous state when in union with gas. Thus carbon, a fixed solid, forms, when in union with oxygen, as has already been mentioned (§ 20), a gas consisting of 12 parts by weight of carbon to 32 of oxygen. This gas, when analyzed, gives rise to a volume of oxygen equal to that of the original gas. The density of this gas is found by experiment to be 22. The density of oxygen is 16. If now one volume of carbon vapour weighing 12 were to unite with one volume of oxygen weighing 16 without condensation, the result would be two volumes of a compound weighing 28, or having the specific gravity 14. But if the two volumes of oxygen (weighing 32) were to combine with one of carbon (weighing 12), and if the three volumes were to contract in combining to two, the result would be a gas having the density of the one actually found, namely, 22. Hence it is supposed that, if carbon could exist in the separate state as a vapour, it "would have" the density 12. Hence 12 is called the *hypothetical density* of carbon vapour.

CHAPTER III.

SYMBOLS AND NOMENCLATURE.

§ 42. The elements (Table, pages 72, 73) have been discovered at various times; by far the greater number within the last hundred years. Bodies such as sulphur, carbon, copper, and many of the metals were known long before it was known that they were elements, and, indeed, before the present meaning of element was conceived.

The familiar names by which they were known are retained. As other elements were discovered, some real or supposed peculiarity of their nature was made use of in giving them names. Such peculiarity was sometimes connected with the physical property of the body[*], or the source whence it was got[†], or some chemical property[‡].

§ 43. *Symbols.*—We have already experienced some of the inconvenience which arises from writing the names of the elements in full. To obviate this they are represented by the initial letters of their names. But as there are more elements than there are letters in the alphabet, it is necessary in some cases to affix to the initial letter some other letter out of their names. Thus carbon, chlorine, cadmium, calcium, chromium, all commence with C. The first is represented by the symbol C, the second by Cl, the third by Cd, the fourth by Ca, the fifth by Cr, &c. In many cases the Latin names of metals are used, and the initial and other letters are employed as symbols. Thus copper (or cuprum) has the symbol Cu, Lead (or plumbum) has the symbol Pb, Silver (argentum) the symbol Ag, &c. As the Latin names of the metals end in *um*, newly discovered metals have for the sake of uniformity received the same termination, as cadmium, thallium, &c.

§ 44. The symbols such as H and Cl, used alone, express simply an indefinite quantity of those elements. When two elements unite to form a chemical compound, the compound is represented by the symbols of its elements put side by side. Thus HCl represents a compound of hydrogen with chlorine. But we have before seen that whenever hydrogen and chlorine unite, they do so in the proportion of 1 to 35·5. Hence the symbol HCl does not only mean a compound of hydrogen with chlorine, but it also expresses that for every 1 unit of weight of hydrogen there are 35·5 of chlorine. Similarly, the body consisting of 12 carbon and 64 or 2 × 32 sulphur, is represented by CSS, C2S, CS^2, or CS_2; the last is the symbol most convenient in use and the one we shall employ. Again, there are two combinations of carbon with oxygen, namely, 12 carbon to 16 oxygen, and 12 carbon to 32 oxygen (or 2 × 16). The first is represented by CO, the second by CO_2. In like manner, the compounds of sulphur with iron (§§ 16, 22, 25) are represented by the symbols FeS, FeS_2, Fe_7S_8. A compound symbol, or symbol of a compound, is called the *Formula* of the compound.

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[*] As bromine, from *bromos*, a stink.

[†] As potassium from potashes or potash.

[‡] As oxygen, from *oxys*, sour.

§ 45. Further, a numeral placed in the same line as the formula implies a multiplication by the numeral of all the subsequent symbols, as far as some mark, comma or bracket, or, wanting this, to the end of the formula. Thus the body alcohol contains and consists of carbon, hydrogen, and oxygen. Its simplest formula is C_2H_6O. It may also be written $O2CH_3$, or C_2H_5HO, and in a variety of other ways. The first of these formulæ, C_2H_8O, which merely expresses the simple numerical relation of the equivalents, is called the *Empirical* formula; the others, which pretend to show something of the arrangement of the elements, knowledge of which may be gathered from the synthesis or analysis of alcohol, are called *Rational* formulæ.

§ 46. When different bodies are to be represented as existing together for any time without chemical change, as when two bodies are placed together in order that they may react upon one another, their symbols or formulæ are joined by the sign +. So, when a chemical action, either synthesis or analysis, gives rise simultaneously to different bodies, the symbols or formulæ of the products are also connected by the sign +.

The chemical change which takes place is shown by an equation whose sides are respectively the symbols or formulæ of the bodies before and after the chemical change. Thus:—

$$C + O = CO$$

$$C + 2O = CO_2$$

$$2C + 3O = CO + CO_2$$

$$\text{(Sugar) } C_{12}O_{11}H_{22} = 12C + 11H_2O, \text{ \&c.}$$

§ 47. Since matter cannot be destroyed nor elements transformed into one another, it follows that there must always be the same number of equivalents of each element after as before the chemical change has taken place.

§ 48. It is sometimes convenient to employ the sign — in expressing a decomposition. Thus

$$C_2H_2O_4 - H_2O = CO + CO_2.$$

Such an equation is of course equivalent to

$$C_2H_2O_4 = H_2O + CO + CO_2.$$

But the first equation shows that the withdrawal of H_2O from $C_2H_2O_4$ gives rise to CO and CO_2, which is the fact; the second might imply that $C_2H_2O_4$ were made out of H_2O and CO and CO_2, which may be the case, but has not yet been done.

We shall henceforth make free use of the symbols of the elements instead of their names; and the student should at once familiarize himself with them. They are all found in the Table, pages 72, 73.

§ 49. *Nomenclature.*—The elements divide themselves naturally into two classes, the metals and the non-metallic elements. The former is by far the most numerous. The principal characteristics of a metal with regard to appearance are its opacity and the great perfection with which a smooth surface of it reflects light. These properties combined, constitute what is called the metallic lustre. Metals in the solid state have different densities, varying from that of the heaviest known body (an alloy of osmium and iridium, sp. gr. $=22{\cdot}6$) to a density less than that of water (lithium $=0{\cdot}594$, being the lightest known solid). All metals may be melted; but mercury is the only unmixed one known in the liquid state at ordinary temperatures. Several (probably all) metals may be converted by heat into vapour, and in that state appear as colourless transparent gases, exactly resembling permanent or hitherto uncondensed gases; so that if some of the permanent gases could be liquefied or solidified, they might be found to have the metallic lustre. One great character of the metals is that they may all, in the liquid state, be mixed with one another, forming alloys; but they all refuse to dissolve in the non-metallic elements or their compounds, unless they first unite chemically with one or more of them.

§ 50. Of the remainder of the elements, the non-metallic ones, a few, O, H, N, and perhaps Fl*, are permanent gases; that is, they cannot be condensed by cold or pressure into liquids or solids. One, chlorine, Cl, is under ordinary circumstances a gas, but can be condensed to a liquid. Bromine, Br, is usually a liquid, but is easily converted into gas by gaining heat, and into a solid by losing it. The rest are more or less easily liquefiable and vaporizable solids, with the exception of carbon (C), boron (Bo), and silicon (Si), which cannot be volatilized or melted when alone.

There are certain elements, such as arsenic (As), which resemble the metals proper in metallic lustre, insolubility, &c., but which are like the non-metallic elements in several of their chemical properties.

§ 51. Beyond the metals proper, whose chemical names all end in *um*, the only systematic termination borne by the elements which shows similarity of property is *ine*, as in chlorine, bromine, &c. The elements oxygen, hydrogen, nitrogen, which all end in *gen*, have little chemical relationship, though as gases they have some physical similarity.

§ 52. When two elements unite together chemically, a compound name is given to the resulting body, a name made up of the names of the elements which the body contains. Thus CO is called the oxide of carbon, FeS the sulphide of iron, and so on.

When two elements unite with one another in more than one proportion, a corresponding variation is made in the name, Latin or Greek numerals being often employed. Thus

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* The properties of elementary fluorine are not yet fully established.

CO is called oxide of carbon (or carbonic oxide).
CO_2 „ binoxide of carbon (or carbonic acid).
FeO „ oxide of iron.
Fe_2O_3 „ sesquioxide of iron (1 to 1½).
Fe_3O_4 „ four-thirds oxide of iron.
CS_2 „ bisulphide of carbon.
PCl_3 „ terchloride of phosphorus.
PCl_5 „ pentachloride of phosphorus.

When the compound body consists of a metal or hydrogen united with a non-metallic body, it is usual to write the symbol for the metal towards the left hand, and to attach the ending *ide* to the name of the non-metallic element. This is a matter of choice, and is not invariably adopted. Thus

FeO, oxide of iron, might be written OFe, ferride of oxygen.
CS_2, bisulphide of carbon, might be written S_2C, carbide of sulphur.

§ 53. The compound of two elements which consists of equal numbers of their equivalents is generally distinguished by the prefix *prot*(*o*) or *mon*(*o*).

Thus FeO is the protoxide of iron.
„ CO „ „ carbon.
„ FeS „ protosulphide of iron.

§ 54. If a metal unites with a non-metallic element in such a way that there is more than one equivalent of the metal for every equivalent of the other element, the prefixes *di* or *sub* are often used. Thus

CuO is the oxide of copper or protoxide of copper.
Cu_2O is the suboxide of copper or dioxide of copper.

§ 55. Sometimes the prefixes *hyper* or *per* are used to denote an excess of the non-metallic element, and the prefix *hypo* a deficiency of it beyond a certain quantity.

§ 56. The terms used by different chemists for the same substance are often different according to the different views they take of the rational composition of it (see § 45); and in very many cases the discovery of new compounds has made the names given to the previously known ones inconsequent. The nomenclature bears the marks of the history of the science, and is a compromise between new and old views. The names of the few bodies which we shall have to consider will be easily acquired as we proceed.

CHAPTER IV.

ACIDS, BASES, AND SALTS.

§ 57. Many compound bodies, consisting of two or more elements, hold one of those elements so loosely that it can be withdrawn and replaced by another element, the remaining elements of the original compound resting undisturbed. The newly introduced element can also be replaced by another, and so on. This is especially the case with a large class of substances containing hydrogen, and which are called *acids*. Such substances usually have, when soluble, a peculiar sour taste, similar to that of lemon-juice or vinegar. They have also the power of changing the colour of certain vegetable colours, turning red such as are blue. The term acid is also frequently, but somewhat improperly, applied to bodies which do not contain hydrogen or other replaceable element, but which, when united with, or even in presence of, water, cause the hydrogen of the water to be replaceable by a metal or similar body*. Examples of such bodies are CO_2, SO_2, &c.

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* We shall find that a group or compound of non-metallic elements may play the same part chemically as a metal.

Examples of acids are:—

HCl.	Hydrochloric acid or chlorhydric acid. It is also called muriatic acid, and is the chloride of hydrogen.
H_2S.	Hydrosulphuric acid or sulphydric acid. It is also called sulphuretted hydrogen, and is the sulphide of hydrogen.
HNO_3.	Nitric acid; also called *aquafortis.*
H_2SO_4.	Sulphuric acid; also called oil of vitriol.
$HClO_3$.	Chloric acid.
$H_2O + CO_2$.	Carbonic acid and water.

The hydrogen of each of these bodies may be replaced by a metal, as potassium, zinc, silver. Thus

	I.		II.		
From	HCl	may be got	KCl,	or $ZnCl_2$,	or $AgCl$.
„	H_2S	„	K_2S,	or ZnS,	or Ag_2S.
„	HNO_3	„	KNO_3,	or $Zn2(NO_3)$,	or $AgNO_3$
„	H_2SO_4	„	K_2SO_4,	or $ZnSO_4$,	or Ag_2SO_4.
„	$HClO_3$	„	$KClO_3$,	or $Zn2(ClO_3)$,	or $AgClO_3$.
„	H_2O, CO_2	„	K_2CO_3,	or $ZnCO_3$,	or Ag_2CO_3.

§ 58. When the hydrogen of an acid has been thus replaced by a metal or similar body, a *salt* is obtained. Thus all the bodies in II. are salts. A salt may therefore be defined as an acid whose hydrogen has been replaced by a metal. It is clear that if the metal of a salt be replaced by a second metal, the same salt is got as if the hydrogen of the corresponding acid had been replaced by the second metal. A salt may be easily, difficultly, or not at all soluble in water. Of the above examples the following are insoluble: ZnS, $ZnCO_3$, $AgCl$, Ag_2S, Ag_2CO_3. Sparingly soluble is Ag_2SO_4; all the rest are readily soluble in water. Soluble salts have a peculiar taste called saline, and resembling that of table-salt, but modified both by the nature of the metal and of the non-metallic part. They are generally solid bodies, and frequently consist of crystals having a very distinct shape, called the "crystalline form."

§ 59. The physical properties of salts, such as their crystalline form, colour, degree of solubility in water, &c. are often so characteristic as to be used in determining what metal is present, or, if this be known, in finding the non-metallic or acid part.

§ 60. Salts, even when soluble in water, often take no effect upon vegetable colours, and are then said to be *physically neutral.* Sometimes only half or other fraction of the hydrogen of an acid is replaced by a metal. When this is the case a *chemically acid* salt results. Such a salt, if soluble in water, generally, but by no means invariably, is also physically acid.

§ 61. It is clear that if any of the above acids which contain water have that water replaced by a metallic oxide, the same salt is got as when the hydrogen is replaced by the simple metal. Thus,

KNO_3 may be got from $2(HNO_3)$ by replacing H_2O by K_2O,
Ag_2SO_4 ,, H_2SO_4 ,, ,, Ag_2O,

and so on. If, in fact, oxide of potassium be added to nitric acid, water is liberated and the above salt is formed; or if oxide of silver is added to sulphuric acid, it replaces the water. This is shown in the following equations:—

$$2(HNO_3) + K_2O = 2(KNO_3) + H_2O.$$
$$H_2SO_4 + Ag_2O = Ag_2SO_4 + H_2O.$$

§ 62. In such a reaction, therefore, from an acid, by the addition of a metallic oxide, we get a salt. The metallic oxide *neutralizes* the acid. A body, very often an oxide, which thus takes the place of water in an acid, liberating and replacing the water and neutralizing the acid, is called a *Base.* The oxides of all metals are bases.

§ 63. When such a body as H_2S or HCl is acted on by a metallic oxide, the sulphide, chloride, &c. of the metal is generally formed, and water is also produced.

$$H_2S + Ag_2O = Ag_2S + H_2O.$$
$$2(HCl) + Na_2O = 2(NaCl) + H_2O.$$

On account of their forming salts (Ag_2S, NaCl, &c.) with metallic oxides, such bodies as HCl and H_2S are called acids, although, unless in the presence of water, they are physically neutral.

§ 64. When more than one equivalent of a base combines with one equivalent of an acid, displacing one equivalent of water, the salt formed is called a basic, or sometimes a *sub*salt.

§ 65. It is evident that the more soluble a metallic oxide is in water, the more readily will it neutralize an acid. Those metallic oxides which are the most soluble in water are called *alkalies*, and their solutions are called *alkaline*. The metals which such alkalies contain are called alkaline metals. The chief of these are potassium and sodium. An alkali, therefore, is a very soluble base.

§ 66. Several acids, especially volatile ones, are readily expelled from their bases. It follows that salts of those acids, especially such as are soluble in water, neutralize acids just as free bases do. Thus

$$H_2SO_4 + Na_2CO_3 = H_2O + CO_2 + Na_2SO_4.$$

Such salts (as Na_2CO_3) are called alkaline salts because, like free alkalies, they turn blue vegetable colours reddened by acids.

§ 67. The names given to the various acids are formed somewhat in the same manner as those composed of two elements, or binary compounds. If, as frequently happens, two non-metallic elements unite in various proportions, more than one of the combinations, in presence of water, has acid properties. Thus P and O unite in two proportions, P_2O_3 and P_2O_5; each of these combines with water and forms an acid.

$$P_2O_3 + 3H_2O = \underset{\text{Phosphorous acid.}}{2(H_3PO_3)}. \qquad P_2O_5 + 3H_2O = \underset{\text{Phosphoric acid.}}{2(H_3PO_4)}.$$

The name of the first ends in *ous*, that of the second in *ic*. And in all cases the termination *ous* implies a less quantity of oxygen than is contained in the corresponding acid whose name ends in *ic*. Thus

H_2SO_3 is sulphurous acid.
H_2SO_4 is sulphuric acid.

§ 68. Frequently more than two combinations of two elements are acids. Thus the body P_2O has acid properties. A name is given to it expressing that it contains less oxygen than phosphorous acid does; it is called hypophosphorous acid. So four of the oxides of chlorine in combination with hydrogen are acids.

$HClO$, hypochlorous acid.
$HClO_2$, chlorous acid.
$HClO_3$, chloric acid.
$HClO_4$, perchloric acid.

§ 69. When water is taken from an acid, or metallic oxide from a salt, neither the one nor the other being replaced, or if in any other way a body is got which *would form* an acid if it combined with water, or *would form* a salt if it combined with a base, that body is called an *anhydrous* acid, or simply an *anhydride*; thus

SO_2 is anhydrous sulphurous acid or sulphurous anhydride.
SO_3 ,, sulphuric acid or sulphuric anhydride.
N_2O_5 ,, nitric acid or nitric anhydride.
CO_2 ,, carbonic acid or carbonic anhydride.

§ 70. The nomenclature of salts stands in a very simple relation to that of acids. An acid containing oxygen whose name ends in *ic* forms salts whose names end in *ate*. An acid containing oxygen whose name ends in *ous* forms salts whose names end in *ite*. Thus

H_2SO_4, sulphuric acid,	forms	$ZnSO_4$, sulphate of zinc.
H_2SO_3, sulphurous acid,	,,	$CuSO_3$, sulphite of copper.
$HClO_4$, perchloric acid,	,,	$Ba2(ClO_4)$, perchlorate of barium.
$HClO_3$, chloric acid,	,,	$AgClO_3$, chlorate of silver.
$HClO_2$, chlorous acid,	,,	$Pb2(ClO_2)$, chlorite of lead.
$HClO$, hypochlorous acid,	,,	$Hg2(ClO)$, hypochlorite of mercury.

§ 71. It is evident therefore that acids are salts of hydrogen —that sulphuric acid is, for instance, the sulphate of hydrogen, nitric acid is nitrate of hydrogen, &c. Acids are hydrogen salts. Anhydrous acids or anhydrides may either combine with water, and so form true acids, or with metallic oxides, and so form metallic salts.

§ 72. Acids which do not contain water, such as hydrochloric acid, HCl, hydrosulphuric acid, H_2S, when they combine with bases, form of course chloride and sulphide, &c., of the metal (§ 63).

§ 73. Many metals, such as magnesium, calcium, potassium, sodium, &c., rarely occur in the uncombined state. They were long known as oxides, and names were given to the salts which those oxides formed with acids. Such names are often retained. Thus

K_2SO_4	is frequently called	sulphate of potash.
$CaSO_4$	,,	sulphate of lime.
$MgCO_3$	,,	carbonate of magnesia.

Such names are not quite systematic; these salts should be, and often are, called sulphate of potassium, sulphate of calcium, carbonate of magnesium.

§ 74. Many compound bodies, besides their chemical names, have familiar ones which are sometimes conveniently used for brevity. Such are water (oxide of hydrogen), saltpetre or nitre (nitrate of potassium), litharge (oxide of lead), lime (oxide of calcium), &c.

The method of symbolization and nomenclature will become familiar as the following chapters are studied.

CHAPTER V.

OXYGEN.

Symbol, O. *Equivalent*, 16. *Density*, 16 (compared with air 1·104). *Solubility* (in water at 0° C.), 100 vols. water dissolve 4·1 vols. of O.

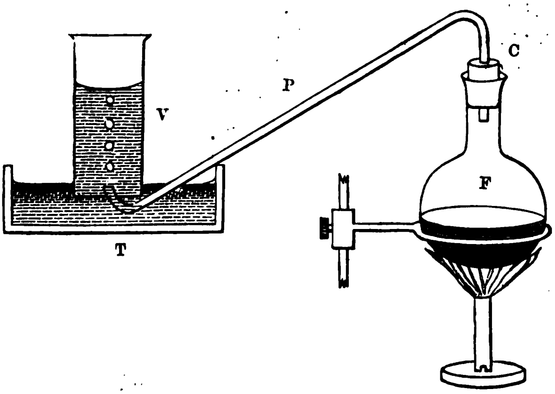
§ 75. Oxygen is the most abundant of all the elements, and forms probably between $\frac{1}{3}$ and $\frac{1}{2}$ of the known globe. It occurs in the air, of which 20 *per cent.* by volume is oxygen, the rest being nitrogen mixed with it. It occurs in water, of which $\frac{8}{9}$ or 88·8 *per cent.* by weight is oxygen, the rest being hydrogen chemically united with it. It occurs in the earth, the crust of which, as far down as has been examined, consists almost entirely of oxides of metals and of non-metallic elements. Most rocks contain about $\frac{1}{3}$ of their weight of oxygen. Oxygen, both as forming a part of water and otherwise, is found in all parts of plants and animals.

§ 76. In order to obtain pure oxygen gas, it is most convenient to heat some substance, either natural or artificial, which contains it, and which is decomposed by heat. Any of the following bodies when strongly heated give up oxygen; the last gives it up mixed with another gas, which, however, can be easily removed.

Protoxide of mercury, HgO, when heated becomes $Hg+O$.
Binoxide of manganese, $3(MnO_2)$, ,, ,, $Mn_3O_4+O_2$.
Chlorate of potassium, $KClO_3$, ,, ,, $KCl+O_3$.
Sulphuric acid, H_2SO_4, ,, ,, H_2O+SO_2+O.

§ 77. If only a small quantity of oxygen is required, it is most convenient to employ chlorate of potassium, a salt manufactured

Fig. 47.



in large quantity. The salt is powdered, mixed with a little binoxide of manganese, which facilitates its decomposition, and heated in a flask F (fig. 47).

The chlorate of potassium on being heated is decomposed into chloride of potassium and oxygen, thus:—

$$KClO_3 = KCl + O_3.$$

The chloride of potassium, together with the undecomposed binoxide of manganese, remains behind in the flask F, while the gaseous oxygen escapes as it is liberated through the tube P, one end of which passes tightly through the cork C of the flask, the other is beneath the surface of water in the trough T. On inverting a vessel V full of water over the end of P as the oxygen is escaping, the gas rises in bubbles, collects in V, and gradually fills it*. Pure oxygen is a colourless gas, without taste or smell; since it forms 20 *per cent.* of the atmosphere, it may of course be breathed with impunity.

§ 78. All bodies which burn in the air, burn with greater energy in oxygen, giving out more light and heat. Burning or combustion in the air is oxidation; so that when a body burns, it or its elements unite with oxygen, and form one or more oxides. Oxygen unites with all metals, forming oxides, some of which are acids, some bases, and some, according to circumstances, are both. It unites also with all non-metallic elements (with the exception, perhaps, of fluorine), frequently in several proportions, and forms with them acids or neutral bodies.

§ 79. The gradual rusting which many metals undergo when exposed to the air, especially to moist air, is a slow process of oxidation. Such metals are called *base* (as distinguished from *noble* metals, which are such as do not spontaneously oxidize). The rust of a metal, therefore, as of iron, zinc, lead, &c., is an oxide of the metal.

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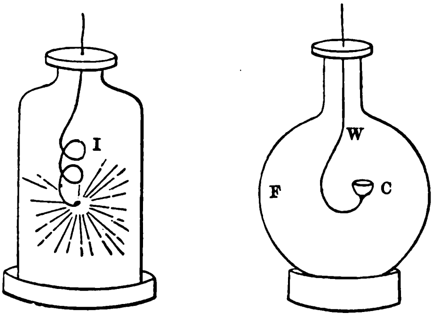
[*] Such an arrangement for collecting a gas is called a "pneumatic trough." The liquid employed in it is sometimes mercury. The gas is said to be collected "over" water or mercury. The apparatus will not require description when again mentioned.

§ 80. If bodies which burn (rapidly oxidize) or slowly oxidize in the air when heated, are heated in pure oxygen, they burn with much greater brilliancy. Thus (fig. 48) if a flask full of oxygen, F, be taken, and by means of a bent wire, W, a little cup, C, containing burning sulphur is introduced, the sulphur burns with great rapidity, giving a beautiful blue light. A fragment of charcoal (carbon) under like circumstances, burns with a splendid white light, while phosphorus gives a magnificent light of almost insupportable brightness. Similarly, if the end of a piece of iron wire, I, be heated red-hot and plunged in the gas, the iron burns (oxidizes, rapidly rusts), giving rise to great light. Oxides of the elements are formed in all cases; but the number of equivalents of oxygen which unite is not always the same. The following equations show the proportion of the elements which unite:—

Fig. 48.



$S+2O=SO_2$, sulphurous acid.
$C+2O=CO_2$, carbonic acid.
$P_2+5O=P_2O_5$, phosphoric acid.
$3Fe+4O=Fe_3O_4$, four-thirds oxide of iron.

The so-formed oxides differ in properties. SO_2 and CO_2 are both gases, and may unite with bases to form salts; they are, therefore, anhydrous acids. P_2O_5 is a snow-white solid, which settles upon the inside of the flask. It also unites with bases, and forms salts (phosphates), and is anhydrous phosphoric acid. The product of the oxidation of the iron, Fe_3O_4, is neither an acid nor a base; that is, it does not unite with acids without decomposition to form salts; it is sometimes called the black or magnetic oxide of iron, being in fact identical with loadstone.

§ 81. Often, when a compound body (that is, one which consists of more than one element) is burnt in oxygen, both or all of its constituent elements are oxidized, and either a mixture or chemical compound of oxides results. Thus, if CS_2, the bisulphide of carbon, be burnt in oxygen, a mixture of carbonic and sulphurous acids is formed.

$$CS_2 + 6O = CO_2 + 2SO_2.$$

If protosulphide of iron be burnt, the result is sulphate of iron.

$$FeS + 4O = FeSO_4.$$

§ 82. When oxygen is required in very large quantity, sulphuric acid, H_2SO_4, is boiled, and its vapour is passed through a porcelain tube heated to whiteness and containing metallic platinum in a finely divided state. It is thereby decomposed into water, sulphurous acid, and oxygen,

$$H_2SO_4 = H_2O + SO_2 + O.$$

The water condenses, and the sulphurous acid is removed by passing the mixed gases over lime, CaO, which combines with the SO_2, forming $CaSO_3$, or sulphite of calcium. The oxygen is then pure.

§ 83. *Ozone.*—When pure dry oxygen is subjected to the action of electric sparks, it shrinks in volume, acquires a peculiar crab-like smell, and possesses a very much greater chemical activity or power of oxidizing; it is then said to be ozonized, or partly converted into ozone. The same body is formed when oxygen is liberated at a low temperature from certain of its compounds. Thus, when binoxide of barium, BaO_2, is acted on by sulphuric acid, the liberated oxygen is ozonized.

$$BaO_2 + H_2SO_4 = BaSO_4 + \text{Ozone} + H_2O.$$

Such modified oxygen is said to be in an *allotropic* state. It consists of no other element but oxygen, and is converted into ordinary oxygen by heat. Ozone is supposed by some to exist in the air. Common oxygen does not decompose iodide of potassium, KI; ozone does so, and sets free the iodine. Free iodine forms a blue colour with starch; so that a mixture of starch-water and iodide of potassium may serve as a test for ozone. If such a mixture be shaken up with a gas containing ozone, the ozone decomposes the iodide of potassium, and the liberated iodine combines with the starch, turning it blue.

§ 84. The tests for oxygen are very simple. It is colourless and tasteless, and requires about thirty times its volume of water for solution. A piece of wood which has been lit and blown out, so as to leave a glowing spark, bursts into flame when introduced into the gas. If a piece of phosphorus be exposed to a gas containing oxygen, even at low temperatures, the phosphorus gradually unites with and withdraws the oxygen. The contraction in volume which the gas undergoes, both shows the presence of oxygen and measures its quantity.

§ 85. The use of the oxygen of the air to plants and animals will be considered in Chapter XVI.

APPENDIX TO CHAPTER V.

NUMERICAL CALCULATION &c.

§ 86. It is indispensable that the student should familiarize himself with the symbols, use of formulæ and equations, equivalents, and the processes of numerical calculation, at as early a stage as possible. This can only be done by setting himself and working out questions similar to the few given below. All the equivalents of the elements which have to be considered in the sequel should at once be committed to memory. They are as follows, with their symbols:—Oxygen, $O=16$; Hydrogen, $H=1$; Carbon, $C=12$; Nitrogen, $N=14$; Chlorine, $Cl=35{\cdot}5$; Bromine, $Br=80$; Iodine, $I=127$; Fluorine, $Fl=19$; Sulphur,

$S=32$; Phosphorus, $P=31$; Silicon, $Si=28$. The equivalents of the other elements may be got as required from Table, p. 72.

Example 1. What weight of oxygen can be obtained from 7 lbs. of chlorate of potassium?

The composition of chlorate of potassium is $KClO_3$, the equivalent of potassium is 39. We have, therefore,

$$\begin{array}{l} K=39 \\ Cl=35{\cdot}5 \\ O_3=\underline{48} \;(=3\times16) \\ \quad\;\; 122{\cdot}5 \end{array}$$

So that 122·5 lbs. of chlorate of potassium contains 48 lbs. of oxygen, all of which it gives up when heated; 7 lbs. will therefore give

$$\frac{7\times48}{122{\cdot}5}\text{ lbs., or }2{\cdot}742\text{ lbs.}$$

Example 2. How much oxide of iron is formed when 20 grammes of iron are burnt in oxygen?

The equivalent of iron is 56, and the chemical reaction is $3Fe+4O=Fe_3O_4$.

$$\begin{array}{l} Fe_3=168\;(=3\times56) \\ O_4=\;\underline{64}\;(=4\times16) \\ \quad\;\;\; 232 \end{array}$$

So that 168 grammes of iron when burnt give rise to 232 grammes of oxide of iron; 20 grammes will therefore give rise to

$$\frac{20\times232}{168}\text{ grms., or }27{\cdot}618\text{ grms.}$$

CHAPTER VI.

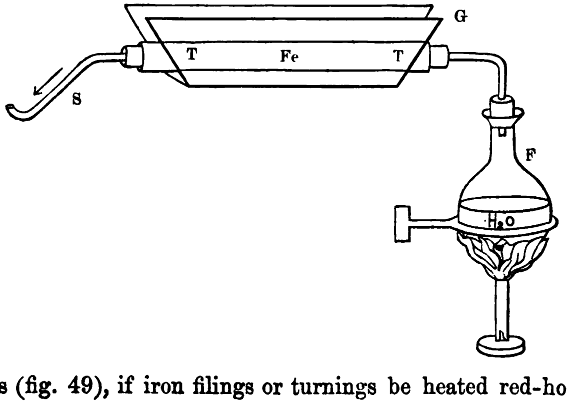
HYDROGEN AND ITS COMPOUNDS WITH THE PRECEDING ELEMENT.

Symbol, H. *Equivalent*, 1. *Density*, 1 (compared with air 0·069). *Solubility* (in water at 0° C.), 100 vols. of water dissolve 0·25 vols. of H.

§ 87. Hydrogen almost always occurs in nature combined with oxygen; with which element it forms water. The great natural sources of hydrogen are therefore the sea, rivers, &c., the moisture of the earth, the vapour of water in the air. Hydrogen is also found in nature combined with carbon, phosphorus, and nitrogen. Hydrogen never occurs in nature in the free or uncombined state. This fact is connected with its affinity for both oxygen and nitrogen, both of which are found abundantly in the free state. It is found in both plants and animals; for water (which contains it) is necessary to all life.

§ 88. Hydrogen is generally obtained by the decomposition of water—that is, by the withdrawal of its oxygen. Bodies which readily oxidize, and whose oxides are fixed, may be employed to combine with the oxygen of the water, and set free the hydrogen.

Fig. 49.



Thus (fig. 49), if iron filings or turnings be heated red-hot in a tube T, which lies in a long charcoal fire contained in G, and steam (vapour of water) be passed over them from the flask F, the iron in T will oxidize, taking the oxygen from the water. The hydrogen will be set free, and escape by the tube S, where it may be collected by the pneumatic trough. The reaction is thus expressed:—

$$\underset{\substack{\text{Water}\\\text{(Steam).}}}{4H_2O} + \underset{\text{Iron.}}{3Fe} = \underset{\substack{\text{Oxide of}\\\text{iron.}}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{H_8}.$$

§ 89. Indeed the oxidation of metals, when exposed to the air, is generally due to the decomposition of the water which exists as vapour in the air, and rarely, or only in part, to the direct union of the metal with atmospheric oxygen.

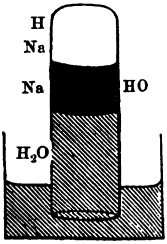
§ 90. Some metals have such a great affinity for oxygen that they rapidly decompose water, in order to oxidize, even at ordinary temperatures. Thus sodium, if thrown into water, decomposes it and forms oxide of sodium, Na_2O, which dissolves in the water, while the hydrogen escapes. The so formed oxide of sodium combines then with a fresh equivalent of water, forming hydrate of sodium. Thus:—

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Sodium.}}{Na_2} = \underset{\substack{\text{Oxide of}\\\text{sodium.}}}{Na_2O} + \underset{\text{Hydrogen.}}{H_2}.$$

$$\underset{\substack{\text{Oxide of}\\\text{sodium.}}}{Na_2O} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Hydrate of}\\\text{sodium.}}}{2(NaHO)}.$$

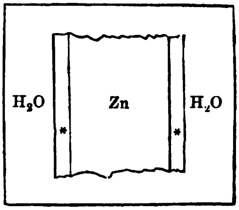
If the sodium be introduced into an inverted tube full of water standing over water, the sodium, being lighter than water, will rise to the top of the tube, and as it decomposes the water (fig. 50) the hydrogen will collect in the upper part of the tube; the hydrate of sodium, NaHO, forming with water a solution heavier than that body, will sink and gradually mix with the water.

Fig. 50.



§ 91. Many metals which decompose water, even when cold, are nevertheless not deeply attacked or rusted by water, because the coating of metallic oxide at first formed, being insoluble in water, forms a water-proof coating or film of oxide which prevents the further oxidation of the metal, and therefore the further decomposition of the water. Such a metal is zinc (fig. 51); the oxide of zinc being insoluble in water.

Fig. 51.



* ZnO

If the oxide be removed as fast as it is formed, a fresh surface of the metal is kept exposed, and the decomposition of the water goes on continually, and is necessarily accompanied by a continual evolution of hydrogen. Oxide of zinc when so formed may be removed by means of sulphuric acid, a body consisting of the elements hydrogen, oxygen, and sulphur, H_2SO_4†. This acid, which is soluble in water, dissolves the oxide of zinc, exchanging H_2 for Zn to form sulphate of zinc, $ZnSO_4$, in doing which water is formed. Thus:—

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Oxide of zinc.}}{ZnO} = \underset{\text{Sulphate of zinc.}}{ZnSO_4} + \underset{\text{Water.}}{H_2O}.$$

So that if zinc, water, and sulphuric acid are brought together, the reaction which ensues may be represented as a continual repetition of the two reactions.

$$Zn + H_2O = ZnO + H_2$$

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O,$$

$$\text{or} \quad Zn + H_2O + H_2SO_4 = ZnSO_4 + H_2O + H_2.$$

It is, however, simpler to view the production of hydrogen as resulting directly and immediately from the replacement of the hydrogen of the sulphuric acid by zinc. Thus:—

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$

§ 92. The apparatus usually employed for the preparation of hydrogen by means of zinc and sulphuric acid is seen in fig. 52. Some scraps of zinc are placed in the bottle W, and covered with water. The bottle W has two necks. Through the cork in the one neck passes the tube T, open at both ends; its lower end is beneath the surface of the water in W. Through the cork of the other neck passes a gas-delivery tube P, leading to the pneumatic trough. When sulphuric acid is poured down the tube T, the resulting hydrogen escapes by the tube P, and may be collected at the pneumatic trough. Many other acids besides sulphuric acid, with many other metals besides zinc, give rise to hydrogen. Thus:—

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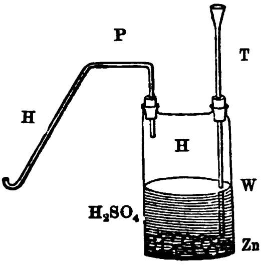
† This body, which is sometimes called oil of vitriol, may be (§ 57) considered the sulphate of hydrogen.

Fig. 52.



$$\begin{aligned} Fe + H_2SO_4 &= FeSO_4 + H_2. \\ Fe + 2HCl &= FeCl_2 + H_2. \end{aligned}$$

§ 93. Hydrogen is the lightest of all known substances, being only $\frac{1}{14 \cdot 5}$ as heavy as air. It is a colourless gas, without taste or smell. It is not an active poison when breathed, but acts injuriously only by depriving the lungs of oxygen (see § 77). It also raises the pitch of the voice, owing to its lightness and small resonance. Hydrogen is seldom used in the arts; it is sometimes employed to inflate balloons, on account of its lightness. Thus 1 *litre* of hydrogen weighs 0·089 *gramme*: 1 *litre* of air weighs 1·293 *gramme*, or 14·5 times as much. So that 1 *litre* of hydrogen will have in the air an ascensional force of 1·293 *minus* 0·089, or 1·204 *gramme*.

§ 94. Hydrogen is sometimes used in the laboratory to reduce or deoxidize certain metallic oxides.

$$MO + H_2 = H_2O + M.$$

Hydrogen has the greatest specific heat of all known bodies. On combining with oxygen it gives rise to a great heat.

§ 95. Hydrogen may be burnt in the air, or combined with oxygen. If a lighted body, as a burning match, be applied to the end of the tube P (fig. 52, § 92), the hydrogen takes fire, it burns or oxidizes; and its oxide is water.

Combinations of Hydrogen with Oxygen.

§ 96. *Water.*—Water is the lowest oxide of hydrogen. It is found abundantly in nature in the solid, liquid, and gaseous state —as ice, water, and steam or vapour.

§ 97. We have seen how water is employed as a source of hydrogen by the removal of its oxygen. Inversely, water may be formed by uniting oxygen with hydrogen. The proportion by weight in which the elements unite is of course that of their equivalents; that is, sixteen parts by weight of oxygen unite with two of hydrogen and form eighteen of water. As both H and O are permanent gases, it is easier to measure than to weigh them. 2 vols. of H are required for every 1 vol. of O; and the gases in uniting contract to two volumes of vapour of water (§ 38), which therefore has the density 9, or, compared with air, 0·6207.

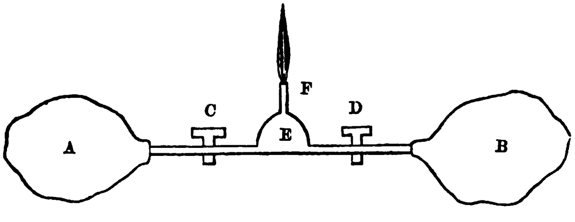
§ 98. The union of oxygen and hydrogen and the formation of water may be effected by simply heating a portion of the mixed gases white-hot. Thus if a bottle be filled with the gases mixed in the above proportion and a light be applied to its mouth, the gases instantly and completely combine with a loud explosion and form water. The heat applied causes the union of the gases which touch it; these, in combining, give out heat, which causes a fresh portion of the two gases to unite, and so on. The progress of the union of the gases through the whole mass of the mixture is so rapid as to appear instantaneous. The great heat produced by the union of H and O expands the vapour of water formed suddenly and greatly; the surrounding air is struck and compressed, and a loud report is the consequence.

§ 99. If an electric spark be made to pass through the mixed gases, they also explode or instantly unite. The same effect is produced if the clean surfaces of certain noble metals are exposed to a mixture of H and O. This is especially the case with platinum in a finely divided state. If a little "spongy" platinum (that is, platinum in a state of minute division) be introduced into a mixture of O and H, it becomes gradually white-hot and the gases explode. The reason of this is not known. The platinum by some means causes the two gases which touch it to condense and unite; and their union gives out heat*.

§ 100. The union of oxygen and hydrogen, or the burning of hydrogen and the formation of water, may also be shown by applying a lighted body to the end of the tube P (fig. 52, § 92) as the hydrogen is issuing from it. The hydrogen takes fire and burns with an almost colourless pale blue flame. If, while doing so, a cold glass jar be held so as to surround the flame, the inside of the jar is found to become coated with a dew of water. This water is derived from the union of the hydrogen with the oxygen of the air.

§ 101. The union of hydrogen with oxygen gives rise to so much heat that it is employed as a means of raising small quantities of bodies to a very high temperature. The apparatus used for this purpose is called the *Oxyhydrogen blowpipe*. Fig. 53 is a sketch, showing the principle of the instrument. The gases H and O are contained in two air-tight bags, B and A, provided with tubes and stopcocks, C and D. The tubes from the bags open into a little chamber, E, where the gases mix. A single tube, F, issues from E. If the cocks C and D are so adjusted and the pressures upon the bags so arranged that twice as much hydrogen

Fig. 53.



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* When a body effects, or alters, or facilitates a chemical change without itself being influenced, as the platinum here and the MnO_2 in § 77, it is said to act by contact. The action is called a Contact-action, or sometimes a *Catalytic* one. The change is called *Catalysis.*

as oxygen, by volume, is delivered. When a light is applied to F the mixed gases unite completely and give out a great heat. If the tube F is wide, the flame will pass down and explode the mixed gases in E; but if it is narrow, its cold metallic sides keep the gases at a lower temperature than that at which combination is possible. The single tube F is generally replaced by a bundle of fine tubes placed side by side. By this means, while the same cooling effect is preserved, more gas may be delivered and a larger flame employed.

§102. Water is also formed when bodies which contain hydrogen are burnt in the air. Thus wood, alcohol, oil, &c. all contain hydrogen; when such bodies are burnt, the hydrogen is oxidized and water is produced.

§ 103. If it is required to know how much hydrogen a substance contains, it is heated with some body which readily parts with oxygen, such as oxide of copper. Water is formed; and $\frac{1}{9}$ of the weight of the water found is the weight of the hydrogen in the original substance.

§ 104. Water is also frequently formed in chemical changes, when the bodies engaged therein contain the elements of water; thus—

$$Ag_2O + 2HCl = 2(AgCl) + H_2O,$$
$$PbO + H_2S = PbS + H_2O, \text{ \&c.};$$

or in the reduction of a metallic oxide by means of hydrogen, as

$$CuO + H_2 = Cu + H_2O,$$
$$Fe_2O_3 + 6H = 2Fe + 3H_2O, \text{ \&c.}$$

It is often liberated from bodies which contain it, as we have seen (§§ 61, 63) to be the case when a hydrated acid is neutralized by a base:

$$H_2SO_4 + PbO = PbSO_4 + H_2O, \text{ \&c.}$$

§ 105. Besides uniting with anhydrous acids, N_2O_5, SO_3, &c., and forming true acids, HNO_3, H_2SO_4, &c., $N_2O_5 + H_2O = 2(HNO_3)$, $SO_3 + H_2O = H_2SO_4$, water also frequently unites with metallic oxides or bases, and especially with such as have energetic basic properties. In such compounds the water may be regarded as playing the part of an acid. Great heat is often set free when water combines in this way with a metallic oxide; and the resulting body is called a *hydrate.*

$$\underset{\text{Oxide of calcium or quick lime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime.}}{CaOH_2O} = \text{hydrate of calcium.}$$

$$K_2O + H_2O = 2(KHO) = \text{hydrate of potassium.}$$

Such water is held by the metallic oxide with great force; the hydrate of calcium requires to be strongly heated before its water is expelled. The hydrate of potassium is not decomposed at a red heat, and, indeed, cannot be said to contain water at all. It is found that metallic oxides which thus combine energetically with water, are also those which are soluble in water or are alkaline (§ 65). The solid hydrate and its solution in water are called *caustic*, and the hydrate of potassium and of calcium are frequently called caustic potash, caustic lime, &c. When metallic oxides combine with water in definite proportions, but with less energy than is the case with the hydrates, the oxides are said to be *hydrated*: thus,

$Fe_2O_33H_2O$ is the hydrated sesquioxide of iron.
$Al_2O_33H_2O$ is the hydrated sesquioxide of aluminium.
$PbOH_2O$ is the hydrated protoxide of lead.

Such compounds frequently give up their water on mere exposure to the air, and always when gently heated.

§ 106. Anhydrous acids, therefore, combine with water to form true acids; metallic oxides combine with water to form hydrates. Towards the acid, the water plays the part of a base, towards the base that of an acid.

§ 107. Water also combines with salts. When a soluble salt is dissolved in water, and the water is gently evaporated away, the salt very often in becoming solid or crystallizing, combines with a certain quantity of water, which it retains with more or less force. Such water is called water of crystallization. Though retained with far less force than the other constituents of the salt, it is quite definite in quantity, and is necessary to the crystalline form which the salt may have. Such water of crystallization is of no especial importance in considering the chemical properties of a salt, because the chemical properties are generally examined in aqueous solution. A salt may unite with water of crystallization in more than one proportion. Thus sulphate of copper, $CuOSO_3$, forms with water

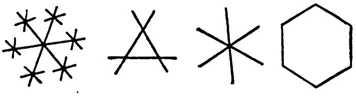
$CuSO_4H_2O$ and
$CuSO_45H_2O$.

So chloride of calcium unites with water in the proportions

$CaCl_22H_2O$ and
$CaCl_26H_2O$.

§ 108. Water in the solid form, or ice, crystallizes in six-sided plates or prisms, and in forms derived therefrom; it melts at 0° C., boils at 100° C., and has a maximum density at 4° C. (See I. § 31). Water will be again considered in Chapter XVII., with especial reference to its occurrence in nature.

Fig. 54.



§ 109. *Binoxide of hydrogen.*—Another oxide of hydrogen, the binoxide, H_2O_2, may be got from the binoxide of barium, BaO_2, by replacing its barium by hydrogen. The binoxide of hydrogen is a colourless, transparent liquid, of a syrupy consistence. It is easily decomposed into water and oxygen. Higher oxides of hydrogen have been supposed to exist; but so little is known about them, that their very existence is doubtful.

CHAPTER VII.

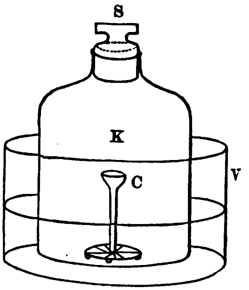
NITROGEN AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, N. *Equivalent*, 14. *Density*, 14 (compared with air 0·965). *Solubility* (in water at 0° C.), 100 vols. of water dissolve 2·03 vols. N.

§ 110. Nitrogen occurs in an uncombined state mixed with oxygen in the air, about 80 per cent. of which by volume is nitrogen. It is also evolved from volcanoes. It is found in nature sometimes in combination with oxygen, sometimes with hydrogen, sometimes with both. It is of course not actively poisonous, forming as it does so large a proportion of the respirable air; but when pure, it causes suffocation on account of the absence of oxygen (see Chapter XVI.). It is necessary to animals, the flesh, tissues, and blood of all animals containing it in combination with other elements. The parts of plants used by animals as food, especially grains, as wheat, barley, oats, &c., contain this element. Although the quantity of *combined* nitrogen in the air is exceedingly small, it plays an important part in the nutrition of plants, and through them of animals.

§ 111. Nitrogen may readily be got in the pure state by removing the oxygen from a quantity of atmospheric air. Thus (fig. 55) a cup of iron, C, is supported in an upright position in a vessel V containing water, and a little phosphorus placed in the cup is heated until it begins to burn or oxidize. A bell-jar, K, having a stopper S, is then inverted over the burning phosphorus, so that its edge is beneath the water in V. The air in K is gradually deprived of its oxygen; and if there is enough phosphorus in C, the whole of the oxygen will be removed and form P_2O_5, which is absorbed by the water. When the action has ceased, the water is found to have risen in the jar so

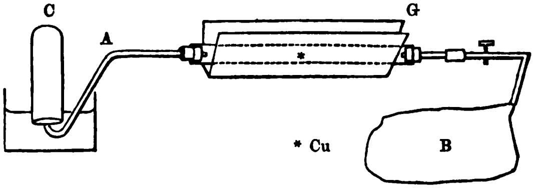
Fig. 55.



as to fill about $\frac{1}{5}$ of it. This shows that the O formed $\frac{1}{5}$ of the air. The remaining $\frac{4}{5}$ are nitrogen.

§ 112. If large quantities of N are required, copper may be used instead of P to remove the oxygen from the air. A higher temperature, however, is required in this case. Copper turnings are placed in a tube T; this is laid along the charcoal furnace G, and heated red-hot; air is slowly forced over the copper from the bag B. The O of the air is arrested by the Cu, and CuO is formed. The N passes along through the tube A, and may be collected at C, or received in an empty bag fastened at A.

Fig. 56.



§ 113. Nitrogen is a colourless and tasteless gas. The distinguishing chemical peculiarity of nitrogen is the great indifference it shows to combine with other bodies. One of the effects of this is that bodies which burn in the air or oxygen cease to burn, or are extinguished in an atmosphere of nitrogen.

Thus, if the stopper S be removed (fig. 55), and burning sulphur, phosphorus, or carbon be brought into the gas, they are at once quenched. Indeed there are very few elements which under any circumstances can be made to unite directly with nitrogen.

§ 114. *Combinations of Nitrogen with Oxygen.*—There are five oxides of nitrogen. Two of them unite with bases and form salts, and are therefore called acids; but only one unites with water to form a definite hydrated acid.

N_2O is nitrous oxide, also called laughing gas.

NO is nitric oxide.

N_2O_3 is nitrous acid, also called anhydrous nitrous acid.

NO_2 is peroxide of nitrogen, also called hyponitric acid, nitrous acid.

N_2O_5 is anhydric nitric acid, also called nitric anhydride.

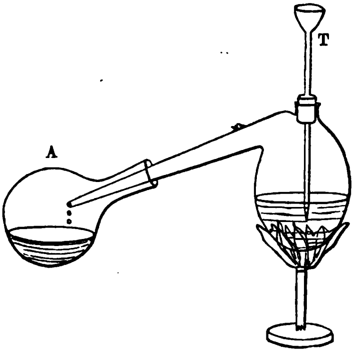
HNO_3 is nitric acid*, also called *aquafortis*.

It is seen that there is a little ambiguity in the nomenclature of these bodies. We shall always employ the names first given.

§ 115. *Nitric acid*, HNO_3.—The most stable oxide of nitrogen is nitric acid. This oxide is formed when animal or vegetable matter containing nitrogen undergoes slow decay in the presence of water and some basic body. In India nitrate of potassium (that is, nitre or saltpetre) is found covering the ground. In South America a similar salt, nitrate of sodium, occurs. Nitrate of potassium, which is used largely in the manufacture of gunpowder, is prepared artificially by mixing dung, stable-refuse, and other matter rich in nitrogen, with a mixture of oxide and carbonate of calcium (old mortar is such a mixture), and exposing in a moist state for some months to the air. The nitrogen gradually oxidizes to N_2O_5, which as formed unites with the lime (oxide of calcium) and forms nitrate of calcium, $Ca2NO_3$. This is afterwards converted into nitrate of potassium by mixing it with carbonate of potassium.

$$Ca2NO_3 + K_2CO_3 = 2KNO_3 + CaCO_3.$$

Fig. 57.



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* $N_2O_5 + H_2O = 2(HNO_3)$.

Carbonate of calcium is formed at the same time, as seen from the equation. Carbonate of calcium is chalk, and, on account of its insolubility in water, may be easily separated from the soluble nitre or nitrate of potassium.

§ 116. Nitric acid is prepared by heating nitrate of potassium with sulphuric acid in a retort (fig. 57). The nitrate of potassium is placed in the retort and sulphuric acid is poured upon it by means of the tube T. The reaction is as follows:—

$$KNO_3 + H_2SO_4 = HNO_3 + HKSO_4.$$

On applying heat to the retort the nitric acid, HNO_3, distils over, and condenses in the receiver A. The sulphate of potassium* remains behind in the retort. So prepared, nitric acid is usually coloured red, on account of the presence of some peroxide of nitrogen, NO_2. The latter may be expelled by boiling or by passing a current of dry air through the liquid; the acid then becomes colourless.

§ 117. Nitric acid has the specific gravity 1·517, and boils at 85°·5 C. It readily gives up a part of its oxygen, and this property constitutes what is called its corrosive power, whence its name *aquafortis*. Most metals are oxidized when in contact with nitric acid; especially if the acid is somewhat diluted with water. The part of the nitric acid which gives up oxygen to the metal is thereby deoxidized; and the resulting lower oxides of nitrogen usually escape as gases, some of which, as we shall see, have a red colour. The oxide of the metal most frequently dissolves in the acid, combines with a fresh undecomposed portion of it, forms water and a nitrate. All nitrates are soluble in water and in dilute nitric acid; hence the metal is seen to diminish or dissolve. The quantity of oxygen lost by the nitric acid in oxidizing the metal depends upon the nature of the metal and upon the temperature.

Nitric acid also acts with energy upon most animal and vegetable matter, destroying their texture, and in many cases dissolving them.

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* $HKSO_4$ is strictly sulphate of potassium and hydrogen.

§ 118. Since all nitrates are soluble in water, it is not possible to test for nitric acid by getting a characteristic precipitate containing nitric acid by the addition of any base. Free nitric acid may be detected by the red fumes which it gives on being heated in the air with metallic copper. Since nitric acid is expelled from bases by sulphuric acid, a body which is supposed to contain nitric acid may be heated with sulphuric acid and copper; whereupon, if nitric acid be present, red fumes will be formed. Nitric acid is most conveniently tested for by mixing the body supposed to contain it with strong sulphuric acid, cooling and pouring upon the mixture a solution of sulphate of iron, $FeSO_4$, in such a manner that the two liquids do not immediately mix. If nitric acid is present, a brown ring is formed where the two liquids come into contact. This is due to the formation of a compound of NO with the sulphate of iron.

§ 119. *Anhydrous nitric acid*, N_2O_5.—This body is prepared by passing the gaseous element chlorine over warm nitrate of silver. Chloride of silver, oxygen, and anhydrous nitric acid are formed.

$$2AgNO_3 + 2Cl = 2AgCl + N_2O_5 + O.$$

Chloride of silver being a non-volatile solid, remains behind. Oxygen and vapour of N_2O_5 pass away. The latter only is condensed by cooling the mixed gases. N_2O_5, or anhydrous nitric acid, is a white solid which melts at 30° C., and boils at 47° C. It unites directly with water, forming common nitric acid, and is by itself very easily decomposed. Its vapour-density has therefore not been determined.

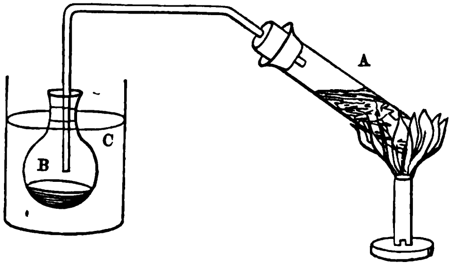
§ 120. *Peroxide of nitrogen*, NO_2.—When dry nitrate of lead, $Pb2NO_3$, is heated it is decomposed into oxide of lead, oxygen, and peroxide of nitrogen, thus:—

$$Pb2NO_3 = PbO + 2NO_2 + O.$$

If the mixed gases are much cooled, the peroxide of nitrogen condenses to a nearly colourless liquid, which boils at 28° C. The oxygen escapes. Fig. 58 shows a simple arrangement for heating the nitrate of lead in the tube A, and condensing the peroxide of nitrogen in the flask B, which is surrounded by a freezing-mixture, C, composed of ice and salt (see I. § 99). Peroxide of nitrogen in the gaseous state has a beautiful red colour.

Peroxide of nitrogen combines directly and without decomposition with some substances, producing compounds resembling those got by the union of chlorine, iodine, &c. with the same substances.

Fig. 58.



§ 121. Peroxide of nitrogen is also got when 1 vol. of oxygen is mixed with 2 vols. of nitric oxide, NO. The two gases contract together to two vols. Now NO consists of equal volumes of N and O united without contraction. Accordingly 2 vols. of NO_2 weigh 16+16+14; or 1 vol. of NO_2 weighs 23 (or 1·587 compared with air).

$$\text{2 vols. of } NO_2 \text{ weigh } \overset{\text{1 vol. oxygen.}}{16} + \overset{\text{2 vols. NO.}}{16 + 14.}$$

§ 122. *Nitrous acid,* N_2O_3.—This, the teroxide of nitrogen, is not known in combination with water, being decomposed by that body. Nitrous acid is obtained by deoxidizing nitric acid by means of the teroxide of arsenic, As_2O_3. Arsenic has two oxides, the teroxide, As_2O_3, and the pentoxide, As_2O_5; both of these are acids; the first is called arsenious, the second arsenic acid. If arsenious acid is warmed with nitric acid it reduces the latter, itself becoming oxidized, thus:—

$$\underset{\text{Arsenious acid.}}{As_2O_3} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Nitrous acid.}}{N_2O_3} + \underset{\substack{\text{Anhydrous}\\\text{arsenic acid.}}}{As_2O_5} + \underset{\text{Water.}}{H_2O.}$$

The anhydrous arsenic acid, however, at once unites with water; thus,

$$\underset{\text{Anhydrous arsenic acid.}}{As_2O_5} + 3H_2O = \underset{\text{Arsenic acid.}}{2H_3AsO_4}.$$

The nitrous acid is volatile and escapes as a gas of a red colour. It may be united with bases, and forms salts called nitrites. Nitrous acid is also formed, but not in so pure a state, by heating nitric acid with starch. Starch contains hydrogen and carbon, which are oxidized at the expense of the nitric acid, reducing it to N_2O_3.

§ 123. Nitrous acid is also formed on mixing 4 vols. of NO (see § 125) with 1 vol. of O. The two gases combine and contract to 2 vols. of N_2O_3. Hence

$$\text{2 vols. of } N_2O_3 \text{ weigh 4 vols. of } NO + \text{1 vol. of O},$$

$$\text{or } \overbrace{\text{2 vols. N} + \text{2 vols. O}}^{\text{4 vols. NO.}} + \text{1 vol. O},$$

$$\text{or } \quad 28 \quad + \quad 32 \quad + \quad 16,$$

$$\text{or 1 vol. of } N_2O_3 \text{ weighs 38 (or 2·61 compared with air).}$$

Nitrous acid at ordinary temperatures is a gas, but may be condensed into a blue liquid at about −35° C. It may be mixed without decomposition with ice-cold water; but warmer water decomposes it into nitric acid and nitric oxide.

$$\underset{\text{Nitrous acid.}}{3N_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitric acid.}}{2HNO_3} + \underset{\text{Nitric oxide.}}{4NO}.$$

§ 124. Nitrite of potassium, from which other nitrites may be got, is obtained by heating nitrate of potassium until $\frac{1}{3}$ of its oxygen is expelled.

$$KNO_3 = KNO_2 + O.$$

§ 125. *Nitric oxide,* NO.—This oxide is a permanent gas; it is formed by gently heating metallic copper with nitric acid diluted with twice its volume of water. The reaction is expressed as follows:—

$$\underset{\text{Nitric acid.}}{8HNO_3} + \underset{\text{Copper.}}{3Cu} = \underset{\text{Nitrate of copper.}}{3Cu2NO_3} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitric oxide.}}{2NO}.$$

§ 126. Nitric acid is a colourless gas; it may be collected over water, in which it is only slightly soluble. It is decomposed with difficulty; most burning bodies, as charcoal and sulphur, are extinguished in it; but phosphorus burns therein with brilliancy, combining with the oxygen and setting free the nitrogen. NO colours sulphate of iron deep brown, owing to the formation of a body of the formula $2FeSO_4, NO$, as we have mentioned in speaking of the tests for HNO_3.

§ 127. The most characteristic property of NO is the eagerness with which it unites with oxygen, forming therewith the red-coloured peroxide of nitrogen already described (§ 121).

$$NO + O = NO_2.$$

In consequence of this property the red fumes of NO_2 are always formed when NO is made in an open vessel exposed to the air. The formation of NO_2, by the direct union of NO with O, serves alike as a test for O and for NO. It is also of very great importance in the manufacture of sulphuric acid.

§ 128. Nitric oxide consists of 1 vol. of nitrogen (weighing 14), united without contraction to 1 vol. of oxygen (weighing 16). The density of the gas is therefore $\frac{14+16}{2}$ or 15, or compared with air 1·034.

§ 129. *Nitrous oxide*, N_2O.—This, the lowest oxide of nitrogen, is formed by heating a body called nitrate of ammonium*, which has the composition NH_4NO_3. Nitrate of ammonium on being heated is decomposed and completely converted into water and nitrous oxide.

$$\underset{\text{Nitrate of ammonium.}}{NH_4NO_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrous oxide.}}{N_2O}.$$

§ 130. Protoxide of nitrogen is a colourless gas, of a sweet taste. 100 vols. of water dissolve 130 vols. of the gas at 0° C.

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* Nitrate of ammonium has very many of the properties of a metallic salt, although it does not contain any metal. The NH_4, ammonium, resembles a metal chemically when in combination with acids. Hence the names of bodies or salts containing NH_4, instead of a metal, are similar to those of true metallic salts. This point will be fully explained in §§ 133–144.

It is much less soluble in warm water. At 0° C. it may be condensed into a liquid by a pressure of about 30 atmospheres. At about —100° C. it solidifies. The gas is composed of 2 vols. of nitrogen (each weighing 14), united with 1 vol. of oxygen (weighing 16) contracted into two volumes. Hence its density, compared with hydrogen, is $\frac{2 \times 14 + 16}{2}$ or 22; compared with air it is therefore 1·517.

§ 131. Nitrous oxide may be breathed with impunity; it produces, however, on some people a more or less reckless hilarity, whence it is also called "laughing-gas." It bears a considerable resemblance to oxygen. Like oxygen it supports the combustion of burning bodies much more freely than air. Phosphorus, carbon, and sulphur burn in it with almost the same brilliancy as they do in pure oxygen—which is remarkable, because they have to overcome the affinity of the nitrogen for the oxygen before they can combine with the latter.

Nitrous oxide is distinguished from oxygen by its degree of solubility in cold water, being at 0° C. 31·7 times as soluble. Again, when oxygen combines with hydrogen, only water is formed, whereas N_2O leaves behind as much N as the volume of the original gas. If potassium be heated with oxygen, K_2O is formed, and the gas wholly disappears; with N_2O, the O is also absorbed, but an equal vol. of N is left. Cold, P gradually absorbs O, but is without action on N_2O.

§ 132. The following Table shows the composition of the various oxides of nitrogen by weight, and the simplest relation of the two constituents N and O by volume. The contraction, if any, is given when known, and the consequent densities of the products.

	Formula.	By weight.		By volume.		Contraction to	Density.
		N.	O.	N.	O.		H=1.
Nitrous oxide	N_2O	28	16	2	1	2 vols.	22
Nitric oxide	NO	14	16	1	1	no contraction.	15
Nitrous acid	N_2O_3	28	48	2	3	2 vols.	38
Peroxide of nitrogen.	NO_2	14	32	1	2	2 vols.	23
Nitric acid........	N_2O_5	28	80	2	5	?	?

Combination of Nitrogen with Hydrogen.

§ 133. *Ammonia*, NH_3.—There is only one known combination of these two elements when alone, namely ammonia, NH_3. This body may be formed in small quantity by passing an electric spark through a mixture of the two gases. 3 vols. of H unite with 1 vol. of N; and in doing so the whole contracts to 2 vols. So that the density of ammonia in the gaseous state is $\frac{14+3}{2}$ or 8·5 (compared with air ·586).

§ 134. Ammonia is abundantly produced when animal or vegetable matter containing nitrogen rots or putrefies * in the presence of water—also when such bodies are heated in closed vessels, especially in presence of strong bases. Hair, feathers, horn, skin, &c. are especially rich in nitrogen. If such substances are heated in closed vessels, and the gases given off are led into water, a pungent liquid is got, called in pharmacy "spirit of hartshorn." This body is a solution of ammonia in water†.

§ 135. Ammonia occurs in immeasurably small quantity in the atmosphere, probably as a carbonate. But, small as is its amount, it is of great importance in furnishing nitrogen to plants (see Chapter XVI).

§ 136. The great source of ammonia at present is the manufacture of coal-gas. The plants which when dead form coal, when living contain nitrogen. Some of this remains in the coal. When coal is heated in closed vessels, as in the manufacture of illuminating gas, the nitrogen unites with the hydrogen of the coal and escapes as ammonia. When the gas is washed by being passed through water, the water absorbs the ammonia and forms what is called the "ammoniacal liquor" of the gas-works.

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* *Decay* is properly used to denote slow oxidation; it may take place either with dry or wet bodies; for decay oxygen is necessary. *Putrefaction* is properly confined to the decomposition which is attended by the formation of living beings—plants or animals. For putrefaction water is necessary. A piece of meat, on being exposed to dry air, will gradually decay, only fat and mineral matter remaining. If exposed to moist air it will putrefy or rot; nearly the same bodies will ultimately be left; but the products formed during the two processes are different.

† It must be remarked that in giving the name to a body, the presence of water is very often neglected. Just as the names tea and coffee are given to the infusions of the solid substances in water, so the name of a chemical compound is very often extended to the same substance dissolved in water, or even combined with it. This we have noticed to be the case with acids, as nitric acid. In a similar way the solution in water of the gas NH_3, ammonia, is also called ammonia.

§ 137. The solution of ammonia in water possesses many of the properties of solutions of metallic oxides in the same liquid. It is caustic to the taste, turns vegetable colours blue, and completely neutralizes acids, forming with them salts very much resembling in colour, crystalline shape, solubility, &c. the corresponding salts of the alkaline metals. Hence the solution of ammonia in water, which is also called ammonia*, is conveniently considered also as an oxide, namely the oxide of NH_4, which is therefore called ammonium. Thus:—

Ammonia .... NH_3.

$$\left.\begin{array}{l}\text{Solution of ammonia}\\ \text{in water, also}\\ \text{called ammonia ..}\end{array}\right\} 2NH_3+H_2O=2NH_4,O=\left\{\begin{array}{l}\text{oxide of am-}\\ \text{monium.}\end{array}\right.$$

§ 138. If oxide of sodium be treated with HCl (see Chapter IX.), common salt or chloride of sodium is formed. Thus:—

$$Na_2O + 2HCl = 2NaCl + H_2O.$$

Similarly, if oxide of ammonium be treated with the same body, chloride of ammonium is formed.

$$2NH_4,O + 2HCl = 2NH_4Cl + H_2O.$$

The chloride of ammonium greatly resembles the chloride of sodium in appearance, taste, &c. Similarly, other salts of ammonium can be formed by neutralizing acids with ammonia (oxide of ammonium). Thus:—

$$2NH_4,O + 2HNO_3 = 2NH_4NO_3 + H_2O,—$$

the products in this case being water and nitrate of ammonium, the latter body being the salt we have already seen employed

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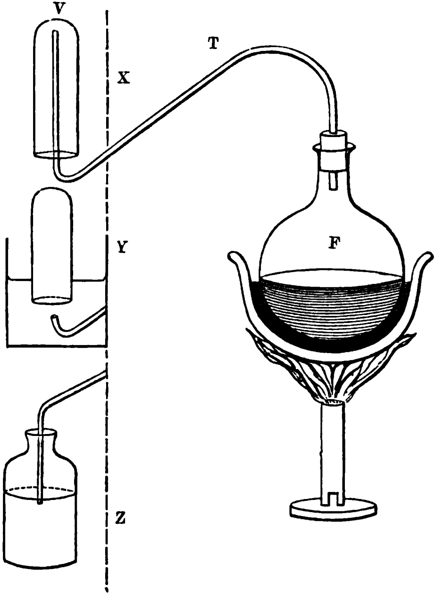
* See note †, p. 123.

(§ 129) as the source of nitrous oxide, N_2O. On account of its volatility and the alkaline nature of its solution, ammonia is sometimes called the volatile alkali.

§ 139. Chloride of ammonium is the salt of ammonium from which the gas ammonia, and the other salts of ammonium, are most usually prepared. Chloride of ammonium, NH_4Cl, is obtained by neutralizing the ammoniacal liquor of the gas-works with hydrochloric acid, and evaporating to dryness, whereupon the chloride of ammonium crystallizes out in small cubic crystals. The same salt was formerly prepared at Ammonia (whence the name) in Asia Minor, by heating camels' dung (containing nitrogen) with common salt (containing chlorine). The chloride of ammonium so formed volatilizes and condenses on the cold surface of the upper part of the oven. This salt, NH_4Cl, bears sometimes the commercial name of "sal-ammoniac."

Fig. 59.



§ 140. When chloride of ammonium is heated with lime (oxide of calcium) or oxide of potassium &c., the metal withdraws the chlorine, water is formed, and the gas ammonia, NH_3, is expelled. The arrangement is seen in fig. 59. Slaked lime (hydrate of calcium, $CaOH_2O$) is mixed with powdered NH_4Cl and a little water in the flask F. On applying heat, the following decomposition takes place:—

$$\underset{\text{Slaked lime.}}{CaOH_2O} + \underset{\text{Chloride of ammonium.}}{2NH_4Cl} = \underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Ammonia.}}{2NH_3}.$$

The gas NH_3 escapes through the tube T, and may be collected (X) by displacement. The end of the tube T is turned up and reaches to the top of the vessel V. Ammonia being lighter than air (§ 133) collects in the tube V, and gradually displaces the air. Or (Y) it is collected over mercury; or (Z) it may be dissolved in water.

§ 141. The composition of the gas ammonia may be shown by leading it repeatedly through a white-hot tube containing copper or iron, or by subjecting it to a series of powerful electric sparks. Every two volumes of ammonia then give rise to 4 volumes of gas, of which 3 are H and 1 is N. Hence (compare § 133) gaseous ammonia is 8·5 times as heavy as hydrogen, or 0·586 the density of air.

§ 142. Ammonia is exceedingly soluble in water. At 0° C. 1 vol. of water dissolves about 1100 vols. of NH_3, and about 730 vols. at 15° C. Ammonia is recognized when in the free state by its peculiar pungent smell (the same smell as that of "sal-volatile," which is the carbonate of ammonia), by its power of turning red vegetable colours blue when moist, and by the dense white clouds which it produces when it meets in the gaseous state with volatile acids.

§ 143. All salts of ammonium are decomposed when heated with oxide of calcium, potassium, or sodium, or the hydrates of those metals, $CaOH_2O$, KHO, or $NaHO$. Hence, in order to see whether a body contains any compound of ammonium, it may be gently heated with water and hydrate of potassium, whereupon the ammonia, if present, will be given off as a gas, and can be recognized by its smell, power of bluing vegetable colours, and fuming when a rod dipped in hydrochloric acid, HCl, or nitric acid, HNO_3, is held near it. The NH_3 as it meets with the HCl or HNO_3 combines with it, and forms minute particles of solid salt in the air; these constitute the clouds; thus:—

$$NH_3 + HCl = NH_4Cl$$
$$NH_3 + HNO_3 = NH_4NO_3.$$

Ammonium in combination is also recognized by the fact that chloride of ammonium, NH_4Cl, forms an insoluble compound with chloride of platinum, $PtCl_4$. If any salt of ammonium is mixed with hydrochloric acid and chloride of platinum, a heavy orange-yellow crystalline precipitate is formed called the platinochloride of ammonium, and having the composition

$$2NH_4Cl, PtCl_4.$$

This body is so insoluble, especially in alcohol, that it is employed for determining the *quantity* of ammonium present. With this exception, and the tartrate, almost all salts of ammonium are soluble in water.

§ 144. Gaseous ammonia, NH_3, may be condensed by great cold or considerable pressure to a colourless liquid; and the liquid may be solidified by a further withdrawal of heat. Thus:—

Under a pressure of 1 atmosphere, NH_3 becomes liquid at —40° C.
,, ,, 7 atmospheres, ,, ,, 15° C.
,, ,, 1 atmosphere, ,, solid —75° C.

§ 145. *Ammonium*, NH_4.—The body which has been above called ammonium (that is, NH_4) cannot be got in the separate state. But a substance having that composition may be readily obtained mixed with mercury on warming a solution of chloride of ammonium with an amalgam of sodium.

$$NH_4Cl + HgNa = NaCl + NH_4Hg.$$

The mercury swells up, increasing to many times its original volume, but preserving its metallic lustre. This substance, which is called "ammonium amalgam," is very instable at ordinary temperatures, breaking up into Hg, H, and NH_3.

CHAPTER VIII.

CARBON AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, C. *Equivalent*, 12. (*Hypothetical*) *density of vapour*, 12 (compared with air 0·828).

§ 146. Carbon occurs in nature in nearly the pure state as crystallized carbon or diamond, a well-known precious stone, found chiefly in the East Indies and in Brazil. Its crystalline forms are the octahedron and forms derived from it. The specific gravity of the diamond is 3·5. It is possessed of a great refractive power for light; this and its rarity make it valued as a gem. In the arts it is chiefly used for cutting glass and abrading hard substances.

Carbon also occurs nearly pure as graphite, plumbago, or black-lead. Its origin in this form is probably due to the action of the internal heat of the earth upon the vegetable matter buried in its crust. Graphite may be prepared artificially by dissolving carbon in hot iron, and letting it separate out as the iron cools.

Carbon may also be got in a state of great purity by decomposing by heat some substances which contain it. Such a form of carbon is lampblack.

It is therefore seen that the same element, carbon, may appear under three entirely different modifications—diamond, graphite, and lampblack.

By no mere physical examination could we conclude that these bodies were the same chemical element, carbon. One similar example we have had in the case of oxygen and ozone; others will appear in the sequel.

Diamond may be converted into graphite, and graphite into soot or lampblack; soot or lampblack may be converted into graphite, but neither lampblack nor graphite has been converted into diamond possessing all the properties of the natural gem.

§ 147. The most familiar form of carbon, in a state of considerable impurity, is coke or charcoal. Wood consists almost exclusively of oxygen, carbon, hydrogen, and metals. When wood is heated in closed vessels, or burnt with partial smothering, as in charcoal-burning, the hydrogen along with part of the oxygen escapes as water, part of the carbon escapes in combination with hydrogen, but a large proportion of the carbon remains behind as a porous mass, called charcoal. This body contains the mineral constituents or metals of the wood. Coal is wood which has been long buried in the earth, and which has lost some oxygen and some hydrogen. When coal is heated out of contact with the air, the carbon which is left behind is very compact, and is called coke. The densities of charcoal, lampblack, and coke depend upon their methods of preparation.

§ 148. Carbon exists also in the air in the form of binoxide of carbon, CO_2, called carbonic acid; the quantity is small, only 0·04 per cent. by volume; but, like ammonia, it plays an important part in the nourishment of plants. Carbon also exists in the earth in great abundance as CO_2, or carbonic acid, combined with bases, as we shall see in considering CO_2.

§ 149. Carbon at ordinary temperatures is almost unalterable in the air. Hence it is used for printers' ink. Carbon in the form of charcoal has a remarkable power of absorbing many gases; and if oxygen be present and the gases be combustible, it effects their combustion, itself remaining unchanged. Hence charcoal is of much use as a disinfecting agent. Most gases which smell offensively contain oxidizable elements. Carbon, in the presence of oxygen, causes the elements of which ill-smelling gases are formed to unite with oxygen and thereby to lose their smell. Putrid bodies lose their smell if rubbed with powdered charcoal; bodies of dead animals, if covered with a few inches of charcoal, give off no disagreeable smell though kept for years. Air is purified if it is breathed through a layer of charcoal; charcoal which is got by burning bones has further the peculiar property (the reason of which is not known) of decolorizing many bodies in the liquid state. It is extensively used for this purpose by the sugar-boiler and -refiner.

§ 150. It will have been gathered from the preceding paragraphs that carbon occurs in the air in combination with oxygen as CO_2 or carbonic acid; it occurs also in the same combination with oxygen in certain rocks, as we shall immediately see. Further, in all plants and animals carbon is found in combination with oxygen and hydrogen.

Compounds of Carbon with Oxygen.

§ 151. Carbon unites with oxygen alone in only two proportions, *carbonic oxide*, CO, and *carbonic acid*, CO_2, both of which are gases.

§ 152. *Carbonic acid* or *carbonic anhydride* (see § 148), the binoxide of carbon, CO_2, occurs in the free state in the air. In every 10,000 volumes of air about 4 volumes are CO_2; that is, CO_2 forms about 0·04 per cent. of the atmosphere. It is given out of the earth into the air by active volcanoes, also from various springs and caverns. The breath and perspiration of animals at all times, the air given out by plants at night, decay, fermentation, artificial burning of wood, coal, gas, &c. are all abundant sources of carbonic acid (see Chapter XVI.). Although the quantity of carbonic acid, CO_2, in the air is so small, it is nevertheless an essential constituent, because it is from the carbonic acid of the air that plants, and through them animals, derive certainly a large part, perhaps the whole of their carbon.

§ 153. Carbonic acid, CO_2, may be prepared by the direct union of the two elements (§§ 15–20). If carbon is burnt in excess of air or oxygen (that is, if there be not less than 32 parts by weight of oxygen to 12 of carbon), the whole of the carbon is converted into CO_2. The same body (carbonic acid) occurs in combination with many metallic oxides, especially oxide of calcium and oxide of magnesium, forming natural carbonates: thus

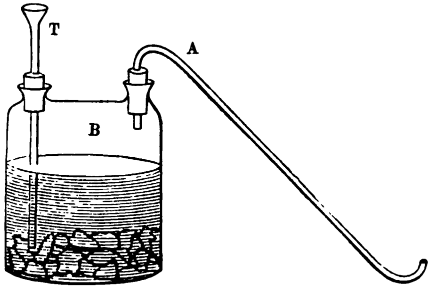
$CaCO_3$ = limestone or chalk.

$MgCO_3$, $CaCO_3$ = magnesian limestone or dolomite.

These natural carbonates form entire mountain-ranges, and therefore afford an immense store of carbon. Marble is a pure and natural crystalline form of carbonate of calcium. Chalk, the fossil remnants of shells, also consists mainly of the same salt. Calcareous, Iceland, or doubly refracting spar is the purest natural form of the same body.

§ 154. Carbonic acid is usually prepared by acting upon carbonate of calcium with almost any acid. It is generally got by treating fragments of marble with dilute hydrochloric acid. The marble is placed in small lumps in a bottle, B (fig. 60), having two necks, and covered with water. Through one of the necks a tube (T) passes, opening beneath the surface of the water. Another tube (A) passes through the second neck and is open just below the cork through which it passes. Hydrochloric acid is poured down the tube T, whereupon the following reaction immediately commences:—

Fig. 60.



$$\underset{\text{Marble or carbonate of calcium.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Chloride of calcium.}}{CaCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid.}}{CO_2}.$$

The carbonic acid may be collected at the end of tube A by displacement (being heavier than air), or at the pneumatic trough. The $CaCl_2$ remains behind in the bottle B.

§ 155. Carbonic acid has the density 22 (or compared with air 1·517). Cold water dissolves about its own volume of the gas. When submitted, at a temperature of 0° C., to a pressure of 28 atmospheres, carbonic acid is converted into a transparent liquid. If a quantity of liquid carbonic acid be allowed to evaporate, so much heat is suddenly absorbed, by the vapour of the evaporating portion, from the residual portion, that the latter becomes solid.

§ 156. Carbonic acid has a slightly pungent sweetish taste. When breathed in the pure state it quickly produces death by suffocation; mixed in small quantities with the air, it acts as a narcotic; in still smaller quantities its action is harmless. As we shall see in Chapter XVI., it occurs in the breath of animals, and its formation in their lungs is essential to their life, and is one of the objects of their breathing. A solution of it in water saturated under pressure is often substituted for "Soda-water." It is found in bread, beer, and sparkling wines, being a product of fermentation—also in foul pits, being a product of decay (§ 134, note).

§ 157. Carbonic acid does not support combustion. Burning carbon, sulphur, wood, phosphorus are extinguished by it; and it has been used to extinguish fires, especially in coal-mines. Carbonic acid may be decomposed by heating in it a piece of the metal potassium. Oxide of potassium is formed, and carbon is set free.

§ 158. Carbonic acid, CO_2, unites directly with metallic oxides or hydrates, and forms carbonates. It is thus immediately absorbed by hydrate of potassium, $2KHO$, forming K_2CO_3, carbonate of potassium. With "lime-water," that is, a solution of hydrate of calcium, $CaOH_2O$, carbonic acid forms a white precipitate of earbonate of calcium, $CaCO_3$, which is insoluble in water. This reaction is almost peculiar to CO_2, and is the most usual test for it. All carbonates are insoluble, with the exception of the carbonates of the alkalies (potassium, sodium, and ammonium).

§ 159. Carbonic acid is expelled from a carbonate by any acid which forms a soluble salt with the base of the carbonate. Carbonic acid is therefore sometimes regarded as a "weak" acid. Its solution in water, however, plays a very important part in nature, on account of the power it enjoys of dissolving almost all rocks. In fact compounds the most insoluble in water are slightly dissolved if the water contain carbonic acid. This solvent power of CO_2 is of great importance to vegetable life; the surfaces of rocks become "weathered" or softened, so that the roots of plants can absorb the mineral constituents needed by them. We shall see in Chapter XVII., especially, that carbonates insoluble in water are soluble in carbonic-acid water.

§ 160. *Carbonic oxide*, CO.—When carbonic acid is passed over red-hot carbon, carbonic oxide is formed, according to the equation

$$CO_2 + C = 2CO.$$

Also, if carbonate of calcium (chalk) and iron-filings are heated together,

$$4CaCO_3 + 3Fe = 4CaO + Fe_3O_4 + 4CO.$$

Further, when a certain acid found in plants and called *oxalic acid* is heated, it is separated into carbonic acid, carbonic oxide, and water; thus:—

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} = CO_2 + CO + H_2O.$$

This reaction takes place with greater ease if some body having a strong affinity for water is present. Oxalic acid is heated in a flask with strong sulphuric acid, which withdraws the water and allows the mixture of carbonic acid and carbonic oxide to escape. The former of these is withdrawn by means of hydrate of potassium, which combines with it, forming carbonate of potassium and leaving the carbonic oxide pure.

§ 161. Carbonic oxide is a colourless gas. It consists of one volume (hypothetical) carbon vapour weighing 12, united with 1 volume of oxygen weighing 16, without contraction. Its density is therefore $\frac{12+16}{2}$ or 14 (compared with air 0·965).

§ 162. Carbonic oxide is an active and violent poison; and to it is attributable the injurious effect which follows breathing the air of a room without a chimney, in which an open charcoal fire is burning. Carbonic oxide burns in the air when heated, and forms carbonic acid. It burns with a blue flame, which may be often seen round the glowing embers of a charcoal fire. Carbonic oxide combines with the subchloride of copper, CuCl, to form a compound,

$$2CuCl, CO, 2H_2O.$$

It unites with potassium and forms

$$KCO.$$

Heated with hydrate of potassium it forms formate of potassium.

Hydrate of potassium + Carbonic oxide = Formate of potassium.

$$KHO + CO = KHCO_2.$$

The formation of these bodies, and its conversion into carbonic acid when burnt, distinguish carbonic oxide from other gases.

Combinations of Carbon with Hydrogen.

§ 163. A great many animal and vegetable substances which contain carbon and hydrogen, give up when heated a portion of those elements in union with one another—that is, as "hydrocarbons." The number of proportions in which carbon and hydrogen unite with one another, even when no other element is present (that is, the number of hydrocarbons), appears to be almost unlimited; no other two elements unite in such various proportions or give rise to such a variety of different compounds. Many scores of such bodies are known; some of them are solid, some liquid, and some gaseous. When organized matter is heated, the hydrocarbons formed are generally various.

§ 164. *Olefiant gas*, C_2H_4, also called "*heavy carburetted hydrogen*, or *ethylen*."—When alcohol is heated with some body having a strong affinity for water, such as chloride of zinc, $ZnCl_2$, or sulphuric acid, the alcohol is decomposed into water and olefiant gas. Alcohol, which is spirits of wine from which the physically mixed water has been removed, still contains the elements of water; its empirical (§ 45) formula is C_2H_6O. If sulphuric acid and alcohol be heated together to a temperature of about 160° C., the following decomposition takes place:—

Alcohol + Sulphuric acid = Ether + Water + Sulphuric acid.

$$2(C_2H_6O) + H_2SO_4 = 2C_2H_5, O + \overline{H_2O + H_2SO_4}$$

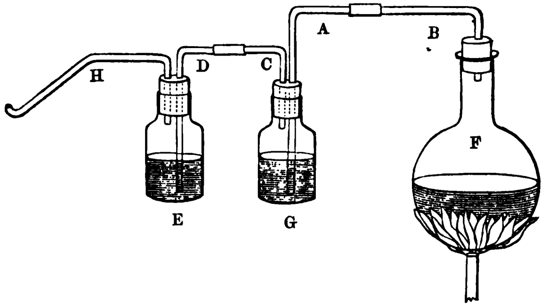
The body $2C_2H_5, O$ is the liquid known as ether or "sulphuric ether." In other words, at the above temperature only one equivalent of water is separated from two equivalents of alcohol. At a higher temperature every molecule of alcohol is decomposed, giving up water:—

Alcohol + Sulphuric acid = Olefiant gas + Water + Sulphuric acid.

$$C_2H_6O + H_2SO_4 = C_2H_4 + \overline{H_2O + H_2SO_4}$$

Besides the C_2H_4 there is also found at the same time some CO_2 and SO_2. Both these bodies being acids may be separated from the olefiant gas by passing the gaseous mixture through hydrate of potassium; any vapour of ether which generally accompanies it having been absorbed by means of strong cold sulphuric acid. The arrangement conveniently adopted to prepare the gas on a small scale is seen in fig. 61. Flask F contains a mixture of alcohol and sulphuric acid made into a paste with sand (to prevent frothing). The gas from F is first led, by means of the tubes B and A, through the "wash-bottle" G, containing strong sulphuric acid, into which the end of the tube A dips. After giving up any vapour of ether in G, the gases pass by means of the tubes C and D into a solution of hydrate of potassium in the second wash-bottle, E. In E the SO_2 and CO_2 are kept back, and the purified olefiant gas is finally delivered through tube H. It may be collected over water or mercury.

Fig. 61.



§ 165. Olefiant gas consists of two volumes of carbon vapour (each weighing 12) united to four volumes of hydrogen (each weighing 1), and condensed to two volumes. The density of the gas is therefore $\frac{2 \times 12 + 4}{2}$ or 14 (compared with air 0·965). 100 volumes of water at 0° C. dissolve about nine volumes of the gas. Olefiant gas may be liquefied by very great pressure. It is colourless, and has a sweet taste.

§ 166. When a light is applied to olefiant gas as it issues into the air, it takes fire and burns with a bright white light, owing to the carbon (which the gas contains in abundance) being heated white-hot by the combustion of the hydrogen (see Chapter XV., Flame). The gas used for illuminating-purposes, and which is obtained by heating coal, wood, oil, &c. in closed vessels (gas-retorts), owes its illuminating power in a great measure to the olefiant gas which it contains. Ordinary coal-gas contains about 4 per cent. by volume of olefiant gas.

§ 167. Olefiant gas unites directly with chlorine, bromine, and iodine, forming bodies of the composition

$$C_2H_4Cl_2, \quad C_2H_4Br_2, \quad C_2H_4I_2.$$

The first of these, $C_2H_4Cl_2$, is a colourless liquid, insoluble in water, and considered therefore by its discoverers to resemble oil. Hence the name, oil-producing or olefiant gas, which C_2H_4 retains. In order that olefiant gas and chlorine may unite, they are led in the moist state into a large globe of glass, which is exposed to the sunshine. The two gases then unite and form the liquid compound, which is purified by washing with water and rectification. Olefiant gas also unites with bromine when the gas is led into the liquid element. The result in this case is also a colourless liquid. When olefiant gas is led over iodine kept at a temperature of 60° C., combination ensues and a white crystalline solid is formed, which is insoluble in water, but soluble in alcohol. Bodies are known having the composition of olefiant gas, united with oxygen and hydrogen; but the gas does not unite directly with these elements.

§ 168. Olefiant gas is absorbed by fuming sulphuric acid (a mixture of H_2SO_4 and SO_3). This property and the above-mentioned reactions with chlorine serve to distinguish it from most other gaseous hydrocarbons. Olefiant gas is also gradually absorbed by sulphuric acid alone, H_2SO_4. On diluting and distilling the solution, the olefiant gas resumes water and is reconverted into alcohol.

§ 169. *Marsh-gas,* CH_4, or "light carburetted hydrogen."—

Vegetable matter, when undergoing spontaneous decomposition in the moist state, gives off a portion of its carbon in union with hydrogen in the form of CH_4. The bubbles which rise on disturbing stagnant ponds on whose bottom vegetable matter is rotting, consist almost entirely of marsh-gas, whence the name which the gas bears. The great masses of vegetable matter which have been buried in the earth and which form coal, have given up a portion of their carbon as marsh-gas. This gas is often retained in a state of compression in the seams of coal; and the latter, when broken by the miner, give out the gas in large quantity. This gas, as it is formed in the coal-mine, is known by the name of "firedamp." Like the preceding gas, marsh-gas or firedamp burns when mixed with oxygen and heated. Hence it sometimes happens that the flame of the miner's lamp ignites the mixture of atmospheric air and firedamp in the mine, causing disastrous explosions (see Chapter XV., Flame). The products of the combustion are, of course, carbonic acid and water; the former is often produced in such large quantity as to suffocate those who have escaped the first explosion of the firedamp. The carbonic acid so formed is known as "chokedamp."

§ 170. Marsh-gas is prepared in a state of purity by heating acetates with alkalies. Acetic acid, which is the acid of vinegar, is a compound of carbon, oxygen, and hydrogen. It is derived from alcohol by the replacement of a portion of the hydrogen of the latter by oxygen. This is, in fact, the change which takes place when wine, beer, &c. turn sour in the process of vinegar-making.

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{H_4C_2O_2} + \underset{\text{Water.}}{H_2O}.$$

The acetic acid, $H_4C_2O_2$, may have its first equivalent of hydrogen replaced by a metal, and forms thereby an acetate; thus $KH_3C_2O_2$ is the acetate of potassium. When acetate of potassium is heated with hydrate of potassium, it is decomposed into carbonate of potassium and marsh-gas; thus:—

$$\underset{\substack{\text{Acetate of}\\\text{potassium.}}}{KH_3C_2O_2} + \underset{\substack{\text{Hydrate of}\\\text{potassium.}}}{HKO} = \underset{\substack{\text{Carbonate of}\\\text{potassium.}}}{K_2CO_3} + \underset{\substack{\text{Marsh-}\\\text{gas.}}}{CH_4}.$$

§ 171. **Marsh-gas** is colourless and tasteless; it results from the union of 1 vol. of carbon vapour weighing 12, with 4 vols. of hydrogen, each weighing 1, condensed to 2 vols. The specific gravity or density of marsh-gas is therefore 8 (compared with air 0·5517). When heated in the air, marsh-gas burns with a bluish flame of feeble luminosity; if previously heated, its light is much more brilliant and becomes yellow. Marsh-gas is one of the chief constituents of coal-gas, which contains about 40 per cent. of it.

§ 172. There is no good test for marsh-gas. It is usually detected and estimated in gaseous mixtures by determining the quantities of carbonic acid and water which are formed when a given volume of the gas is completely burnt.

Compound of Carbon with Nitrogen.

§ 173. *Cyanogen*, CN.—This body cannot be here closely examined, although its compounds are numerous and important. The two elements, carbon and nitrogen, when united in the above proportion, form a group which behaves very much as a single element, and closely resembles, chemically, chlorine, bromine, and iodine (see Chapter IX.). For this reason a distinct name and symbol is generally given to it.

$$\text{Cyanogen} = CN = Cy.$$

§ 174. When animal matter, rich in nitrogen, as leather, horn, &c., is heated red-hot with carbonate of potassium and metallic iron, a complicated reaction takes place, resulting in the formation, amongst other products, of a compound of potassium, iron, and cyanogen, which is obtained on treating the cold mass with water and crystallizing. This body has the composition

$$4KCy, FeCy_2; 6H_2O \text{ or } K_4FeCy_6, 6H_2O,$$

and is known in commerce as the "yellow prussiate of potash," or ferrocyanide of potassium. It is manufactured on a large scale, being the source of "prussian blue," and is extensively used in dyeing. The water which the crystallized salt contains may be removed by heat.

§ 175. If the ferrocyamide of potassium be fused with carbonate of potassium, it is wholly converted into cyanide of potassium and carbonate of iron, according to the equation

$$\underset{\text{Ferrocyanide of potassium.}}{K_4FeCy_6} + \underset{\text{Carbonate of potassium.}}{K_2CO_3} = \underset{\text{Cyanide of potassium.}}{6KCy} + \underset{\text{Carbonate of iron.}}{FeCO_3}.$$

The fused cyanide of potassium is poured off from the subsided carbonate of iron upon a cold surface, whereupon it solidifies into a marble-like mass. It may be purified by solution in alcohol. Cyanide of potassium is a powerful poison; it is extensively used in photography. It is employed largely in the laboratory as a "reducing agent," having at high temperatures a great affinity for oxygen, which converts it into the *cyanate* of potassium, $KCyO$.

§ 176. When cyanide of potassium is treated with sulphuric acid, *hydrocyanic* acid, also called prussic acid, is obtained.

$$2KCy + H_2SO_4 = K_2SO_4 + 2HCy.$$

Hydrocyanic acid, HCy, is a transparent gas, which may be condensed by cold or pressure into a transparent liquid. Hydrocyanic acid dissolves very abundantly in water. The acid itself, and all soluble cyanides, are violent poisons, and are used in small doses in medicine.

§ 177. Cyanogen itself is obtained from the cyanide of mercury by heat. The salt is decomposed into mercury and cyanogen.

$$HgCy_2 = Hg + 2Cy.$$

In this decomposition a part of the cyanogen undergoes a change, being converted into "paracyanogen," a body which has the same chemical composition as cyanogen, but different physical properties, being a fixed solid. Cyanogen is a colourless gas of peculiar suffocating smell, and is very poisonous. 100 volumes of water dissolve about 400 volumes of cyanogen. Cyanogen consists of 1 vol. of carbon weighing 12, united to 1 vol. of nitrogen weighing 14, the whole condensed to 1 volume. Its density is therefore 12+14 or 26 (compared with air 1·79). Cyanogen may be burnt in the air, and gives a purple flame; the carbon only burns.

CHAPTER IX.

CHLORINE AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, Cl. *Equivalent,* 35·5. *Density,* 35·5 (compared with air 2·448).

§ 178. *Chlorine* exists abundantly in the sea as chloride of sodium, $NaCl$ (common salt), chloride of magnesium, $MgCl_2$, &c.,—and in a few minerals as chloride of silver, $AgCl$, &c. Masses of mineral salt, rock-salt, are also found in the earth, having been probably deposited from sea-water. Chlorine is never found in the free state in nature. This is owing to its great affinity for hydrogen and the metals. Its affinity for hydrogen is so great that it will expel oxygen from water in order to combine with its hydrogen. Hence, owing to the universal distribution of water, chlorine is never found in the elementary state.

§ 179. Chlorine unites with all the known elements (excepting perhaps fluorine, see Chapter XI.), forming chlorides; and it is from some of these chlorides that chlorine itself may be procured. Some metallic chlorides when heated give up the whole or part of their chlorine. Others will bear a red heat without decomposition; other metallic chlorides are volatile without decomposition.

§ 180. The readiest way of preparing chlorine is by removing the hydrogen from the chloride of hydrogen, HCl, or hydrochloric acid. Hydrochloric acid is formed, as we shall see (§ 192), when chloride of sodium, $NaCl$, and sulphuric acid act upon one another,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

the products being sulphate of sodium and hydrochloric acid. The HCl dissolves in water and forms what is known as "spirit of salt," "muriatic acid," or hydrochloric acid. If hydrochloric acid be brought into contact with certain bodies containing abundance of oxygen, it loses hydrogen, and the chlorine is liberated. Binoxide of manganese, MnO_2, as we have already learnt (§ 76), is such a body ready to give up a part of its oxygen. On warming hydrochloric acid and binoxide of manganese together, the following reaction takes place:—

$$4HCl + MnO_2 = 2H_2O + MnCl_2 + 2Cl.$$

There are therefore formed water, chloride of manganese, and chlorine.

§ 181. Instead of hydrochloric acid and binoxide of manganese, we may employ a mixture of chloride of sodium, sulphuric acid, and binoxide of manganese, because the first two of these give rise to sulphate of sodium and hydrochloric acid (according to the first equation in § 180), which latter acts upon the binoxide of manganese (according to the second equation in § 180). The whole reaction in this case may be represented thus:

$$\underset{\text{Chloride of sodium.}}{2NaCl} + \underset{\text{Binoxide of manganese.}}{MnO_2} + \underset{\text{Sulphuric acid.}}{2(H_2SO_4)} = \underset{\text{Sulphate of manganese.}}{MnSO_4} + \underset{\text{Sulphate of sodium.}}{Na_2SO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl.}$$

In order to remove traces of hydrochloric acid which accompany the gas, the chlorine is made to bubble through a wash-bottle containing water. If it is required dry, it passes through a second similar wash-bottle containing sulphuric acid. Chlorine dissolves in, and gradually decomposes water; and it immediately combines with mercury. It cannot, therefore, be collected over either of these liquids; but being more than twice as heavy as air, it may be collected by downward displacement.

§ 182. Chlorine may be obtained in the liquid form by subjecting it to great pressure or great cold. At 16° C it becomes liquid under a pressure of 4 atmospheres, and then appears as a yellow liquid of the density 1·3.

§ 183. The properties of chlorine are very well marked. A greenish-yellow gas of peculiar penetrating smell, it acts injuriously upon the respiratory organs even when largely diluted with air, in a pure state producing instant suffocation. It dissolves readily in water, which at ordinary temperatures takes up between two and three volumes of the gas, producing a solution called chlorine-water. It combines directly and eagerly with most metals, giving rise to chlorides, the formation of which is often attended by light.

§ 184. When in the free state it is detected by the power it has of expelling iodine from iodides (see §§ 207–208), and by the blue colour which the so liberated iodine imparts to starch. Bromine and some of the oxides of nitrogen, however, enjoy the same property as chlorine in this respect. If chlorine be shaken up with water containing zinc in a finely divided state, the zinc unites with the chlorine and forms chloride of zinc, $ZnCl_2$, which is soluble in water. If this chloride of zinc be treated with nitrate of silver, $AgNO_3$, nitrate of zinc and chloride of silver are formed.

$$ZnCl_2 + 2AgNO_3 = Zn2NO_3 + 2AgCl.$$

The latter body, chloride of silver, is a white curdy body, insoluble in water, insoluble in nitric acid, but easily soluble in ammonia.

§ 185. Chlorine is largely employed as a bleaching agent. Flowers and most vegetable colours, exposed to the action of chlorine, become white. As a bleaching agent, free chlorine is usually employed as a solution in water. Chlorine is also employed in the manufacture of "bleaching powder" and "disinfecting powder." These important substances are obtained by passing chlorine over lime, magnesia, &c.; and that got when lime is used is called chloride of lime.

$$\underset{\text{Lime.}}{2CaO} + \underset{\text{Chlorine.}}{4Cl} = \underset{\text{Bleaching powder.}}{CaCl_2, CaCl_2O_2}.$$

The composition of bleaching powder is therefore that of a feebly united double salt, chloride of calcium, $CaCl_2$, united with $CaCl_2O_2$, which, as we shall see immediately (§ 188), is hypochlorite of calcium. The empirical formula of bleaching powder may be, and often is, written $CaOCl_2$, which expresses the same ratio between the elements as the above rational formula. When bleaching powder is exposed to the air, the carbonic acid of the air gradually decomposes the hypochlorite of lime, forming carbonate of calcium, and setting free hypochlorous acid.

$$CaCl_2O_2 + CO_2 = CaCO_3 + Cl_2O.$$

The latter product, hypochlorous acid, Cl_2O, destroys many kinds of organic matter (colouring-matter, miasma)—its oxygen forming carbonic acid with the carbon thereof, and the chlorine forming hydrochloric acid with the hydrogen.

§ 186. All chlorides are soluble in water, excepting AgCl, $PbCl_2$, and HgCl.

Compounds of Chlorine with Oxygen.

§ 187. There are three anhydrous oxides of chlorine:—

Cl_2O, anhydrous hypochlorous acid;
Cl_2O_3, anhydrous chlorous acid;
ClO_2 or Cl_2O_4, peroxide of chlorine.

The first two of these form hydrogen acids, as do also two higher oxides; thus:—

HClO, hypochlorous acid;
$HClO_2$, chlorous acid;
$HClO_3$, chloric acid;
$HClO_4$, perchloric acid.

Of these five oxides and acids we need only consider (1) Cl_2O and HClO, (2) $HClO_3$, (3) $HClO_4$.

§ 188. *Hypochlorous acid*, Cl_2O, is prepared by passing dry chlorine over dry oxide of mercury which is kept cold; thus:—

$$HgO + 4Cl = HgCl_2 + Cl_2O.$$

Hypochlorous acid is a deep-red liquid, easily decomposed by heat, and then violently exploding. It boils at 24° C and mixes in all proportions with water. A solution of it in water may be easily made by passing chlorine into *cold* caustic potash (hydrate of potassium), carbonate of potassium, phosphate of potassium, &c.; thus:—

$$KHO + 2Cl = KCl + HClO.$$

On gently warming, the HClO passes over, and may be collected in water.

§ 189. *Chloric acid*, $HClO_3$.—If chlorine is passed into a hot concentrated solution of hydrate of potassium, the chlorine combines with the potassium, partly as chloride, partly as chlorate.

$$6KHO + 6Cl = 5KCl + KClO_3 + 3H_2O.$$

The chlorate of potassium being less soluble in water than the chloride, separates out as white tabular crystals. Chlorate of potassium is the only important salt of chloric acid. It is often used as an oxidizing agent, on account of the readiness with which it parts with oxygen. Thrown into warm strong sulphuric acid it explodes with violence, because the liberated chloric acid can only exist without water at a low temperature. A dilute solution of chloric acid may be got by adding sulphuric acid to a solution of chlorate of barium. The sulphate of barium which is thereby formed is insoluble and sinks down; the solution of chloric acid may be decanted therefrom. All chlorates are soluble in water.

§ 190. *Perchloric acid*, $HClO_4$, is got, in combination with oxide of potassium, by heating chlorate of potassium until only a portion ($\frac{2}{6}$ or $\frac{1}{3}$) of its oxygen is expelled; thus:—

$$2KClO_3 = KCl + KClO_4 + 2O.$$

The residue, consisting of a mixture of chloride of potassium and perchlorate of potassium, is treated with a little cold water, which dissolves the chloride of potassium. The perchlorate is finally purified by recrystallizing it from boiling water. Perchloric acid in combination with water may be prepared by treating perchlorate of barium with sulphuric acid. It is much more stable than chloric acid.

Combination of Chlorine with Hydrogen.

§ 191. *Hydrochloric acid*, HCl, *also called muriatic acid or chlorhydric acid.*—This important body may be formed by the direct union of its elements. If equal volumes of chlorine and hydrogen be heated red-hot or exposed to the direct sunlight (sunshine), they combine completely and with explosive violence, giving rise to hydrochloric acid, HCl, which, when cool, occupies the same volume as the original gases. The density of hydrochloric acid is therefore $\frac{35{\cdot}5+1}{2}$ or 18·25 (compared with air 1·258). Even diffuse daylight and artificial light effect, according to their intensity, the more or less rapid formation of hydrochloric acid out of its elements, and a mixture of equal volumes of the gases has been used as a photometer* or light-measurer.

§ 192. Hydrochloric acid, however, is more conveniently prepared by treating chloride of sodium with sulphuric acid; the reaction which takes place varies according to the relative quantities of the substances employed.

$$\underset{\text{Chloride of sodium.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphate of sodium.}}{Na_2SO_4} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

Or, if half the quantity of chloride of sodium is employed,

$$NaCl + H_2SO_4 = \underset{\text{Acid sulphate of sodium.}}{HNaSO_4} + HCl.$$

The second of these reactions is the one generally used in the laboratory; it requires little or no aid from heat. The first is employed in manufacture; it requires a high temperature, but economizes the sulphuric acid.

Sulphate of sodium is extensively employed in the manufacture of carbonate of sodium; and it is from this manufacture that the hydrochloric acid of commerce is chiefly derived, according to the above equation.

§ 193. Hydrochloric acid is a colourless gas, of suffocating acid smell; it fumes in moist air, on account of its combining with the water therein. The gas is eagerly absorbed by water; and the hydrochloric acid, or "muriatic acid," or "spirit of salt" of commerce is a solution of the gas in water. Water at 4° C. absorbs about 470 times its volume of the gas; 100 volumes of water dissolve 47,000 volumes of HCl. If this solution be boiled, it at first gives off the pure gas, but afterwards distils at about 112° C. The composition of the acid distilled depends upon the pressure to which it is subject during distillation.

§ 194. Hydrochloric acid in solution attacks a large number of the metals (as iron, zinc, tin, aluminium), forming chlorides and evolving hydrogen. It also attacks, and generally dissolves, metallic oxides, forming the corresponding chlorides and water,

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* Or more properly actinometer, "the actinic rays" being the name given to that part of light which in this and many other cases affects the chemical force.

$Zn + 2HCl = ZnCl_2 + 2H.$ $ZnO + 2HCl = ZnCl_2 + H_2O.$
$Fe + 2HCl = FeCl_2 + 2H.$ $CaO + 2HCl = CaCl_2 + H_2O.$
$Sn + 2HCl = SnCl_2 + 2H.$ $SnO + 2HCl = SnCl_2 + H_2O.$

On this account hydrochloric acid is often used in order to bring metals or their oxides into a state of solution previously to their examination.

§ 195. Hydrochloric acid and soluble chlorides are detected by the formation of the insoluble chloride of silver when they are mixed with a soluble salt of that metal (§ 184). The chloride of silver is insoluble in all acids, but soluble in ammonia.

Compounds of Chlorine with Carbon.

§ 196. There will probably be found as many chlorides of carbon as there are hydrocarbons. They are usually got by the action of chlorine upon hydrocarbons, assisted by the light of the sun.

$$C_mH_n + 2nCl = C_mCl_n + nHCl.$$

One part of the chlorine in such cases replaces the hydrogen, and another part of the chlorine unites with it. One may very often obtain an intermediate product in which only a part of the hydrogen is replaced; thus:—

$$C_mH_n + nCl = C_mH_{\frac{n}{2}}Cl_{\frac{n}{2}} + \frac{n}{2}HCl, \&c.$$

It is clear that there may be a very great many more of such chloro-hydrocarbons than there are of hydrocarbons alone.

§ 197. Chlorine combines with carbonic oxide in the direct sunlight, and produces a gas called *phosgene gas,* of which the composition is $COCl_2$. Equal volumes of the gases unite, and they contract in doing so to one volume. The density of this gas is therefore 49·5 (compared with air 3·414). It is called also chlorocarbonic acid. When in contact with water it is decomposed into carbonic acid and hydrochloric acid.

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

Compounds of Chlorine with Nitrogen.

§ 198. *Chloride of ammonium,* NH_4Cl, which consists of the three elements, has been already sufficiently described under ammonia (§§ 133–145). If this body be submitted to the action of chlorine, some, perhaps all the hydrogen of the NH_3 may be replaced by chlorine, and an oily, highly explosive body be obtained, the so-called chloride of nitrogen.

CHAPTER X.

BROMINE AND IODINE, AND THEIR COMPOUNDS WITH THE PRECEDING ELEMENTS.

Bromine.

Symbol, Br. *Equivalent,* 80. *Density of vapour,* 80 (compared with air 5·517).

§ 199. Bromine is a widely distributed but by no means abundant element. It is found in nature as an insoluble bromide of silver, AgBr. But its chief source is the sea (which contains a very small quantity of it) and certain mineral springs (from which it is also sometimes extracted). In both cases it is found as bromide of magnesium, $MgBr_2$, a very soluble salt; so that when the less soluble salts, chloride of sodium, sulphate of magnesium, &c., have been separated by concentrating the brine, the bromine is found in the " mother-liquor " or liquid residue.

§ 200. A current of Cl is passed through the " mother-liquor " of sea-water; the chlorine forms chloride of magnesium with the magnesium, expelling the bromine, which dissolves in the water, deepening it in colour. The aqueous solution is then agitated with ether, which dissolves the bromine and rises with it to the surface of the liquid. The etherial solution is then decanted and shaken with a solution of hydrate of potassium. The bromine combines with the potassium partly as bromide, and partly as bromate of potassium,

$$6Br + 6KHO = 5KBr + KBrO_3 + 3H_2O,$$

both of which dissolve in the water, while the ether is decolourized, and may be again employed for a similar purpose. On evaporating the aqueous solution of KBr and $KBrO_3$ to dryness, and heating, the $KBrO_3$ parts with the whole of its oxygen,

$$KBrO_3 = KBr + O_3,$$

so that the residue consists entirely of KBr. This salt, the bromide of potassium, is used extensively in photography, and also in medicine. From bromide of potassium, bromine may be prepared by a method quite similar to that employed (§ 181) in the preparation of chlorine, thus:—

$$2KBr + MnO_2 + 2(H_2SO_4) = K_2SO_4 + MnSO_4 + 2H_2O + 2Br.$$

The bromine passes over as a reddish-black liquid of extremely pungent smell. Its density is about 2·96. It boils at 63° C., and freezes at $-7°$ C. Exposed to the air, it evaporates, giving a red vapour.

Combination of Bromine with Oxygen.

§ 201. *Bromic acid*, Br_2O_5 (only known in combination).—The most important oxide of bromine is bromic acid, Br_2O_5, corresponding with chloric acid. Bromate of potassium is prepared in a way precisely similar to that used to make chlorate of potassium (§ 189), which body it closely resembles—namely, by treating a hot solution of hydrate of potassium with bromine. The free acid dissolved in water is formed by treating bromate of barium with sulphuric acid. Its formula is $HBrO_3$.

Combination of Bromine with Hydrogen.

§ 202. *Hydrobromic acid*, HBr.—This body cannot be formed similarly to hydrochloric acid, because, if a bromide is treated with strong sulphuric acid, bromine is set free, and part of the sulphuric acid is reduced to sulphurous acid; thus:—

$$2KBr + 2H_2SO_4 = K_2SO_4 + 2H_2O + 2Br + SO_2.$$

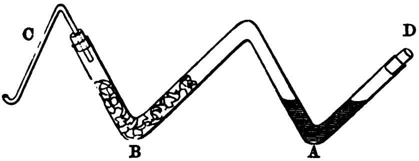
It may be prepared in solution by precipitating the barium out of bromide of barium by means of dilute sulphuric acid.

$$BaBr_2 + H_2SO_4 = \underset{\text{(insoluble.)}}{BaSO_4} + 2HBr.$$

But it is best formed by decomposing the bromide of phosphorus (§ 274), PBr_3, by water.

Fig. 62 shows a convenient arrangement for this purpose. A glass tube, A B, is bent in the form of a letter W. In the bend B are placed a few pieces of phosphorus, together with some pounded glass and a little water. A little bromine is poured into the bend A; the end D is then corked, and a gas-delivery-tube, C, fastened to the opposite extremity. On inclining the tube so that a little bromine runs from A into the bend B, it immediately unites with the phosphorus and forms PBr_3, which, however, is instantly decomposed, by the water clinging to the pounded glass, into phosphorous acid and hydrobromic acid.

Fig. 62.



$$PBr_3 + 3H_2O = 3HBr + H_3PO_3.$$

Hydrobromic acid is a colourless gas freely soluble in water. It consists of equal volumes of hydrogen and bromine vapour united without condensation. Its density is therefore $\frac{80+1}{2}$ or 40·5 (compared with air 2·79).

§ 203. Free bromine is detected by the power it has of turning starch brown; if the bromine is present as a bromide, some chlorine gas must be added to set it free. Hydrobromic acid and soluble bromides give an insoluble precipitate of bromide of silver when mixed with a solution of silver.

$$KBr + AgNO_3 = AgBr + KNO_3.$$

The bromide differs from the chloride of silver (§ 184) in being very much less soluble in ammonia. Bromide of silver is decomposed by chlorine, bromine being liberated. Chloride of silver is, of course, unacted on by chlorine.

§ 204. *Bromine* and *chlorine* unite when brought into contact, and form a yellow liquid soluble in water. Other compounds of bromine with the preceding elements need not be considered.

Iodine.

Symbol, I. *Equivalent*, 127. *Density of vapour*, 127 (compared with air 8·76).

§ 205. Iodine occurs, in very minute quantity, in sea-water. Marine plants collect from the sea the salts containing iodine; so that the ashes of seaweed contain iodine, chiefly as iodide of sodium.

§ 206. The sun-dried seaweed is burnt in shallow pits at as low a temperature as possible; the ash is called *kelp*. This is treated with boiling water, and the soluble part, containing the iodine as iodide of sodium, is evaporated; whereupon the less soluble salts crystallize out and are removed; these are chiefly carbonate and sulphate of sodium, and chloride and sulphate of magnesium. The mother-liquor, containing NaI, is treated with sulphuric acid, and after standing some time is mixed with MnO_2, and heated in a leaden retort. The reaction is quite similar to that attending the formation of chlorine (§ 181), namely,

$$2NaI + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + 2I.$$

The iodine distils over as a beautiful violet-coloured vapour which condenses in the receiver in brilliant purplish-black scales of an almost metallic lustre.

§ 207. Iodine is insoluble in water, but it dissolves abundantly in a solution of iodide of potassium, as also in alcohol, ether, bisulphide of carbon, &c. Iodine has a not unpleasant faint smell, similar to that of chlorine. It stains the skin of a yellow colour. Its density is 4·95; it melts at 113° C., and boils at 180° C., producing a deep-violet vapour. Iodine, as a solution in alcohol, and also as iodide of potassium, is a valuable medicine against glandular affections. Iodide of potassium is also much used in photography. Iodine combines with the same metals as chlorine and bromine combine with, but generally with a less amount of force than is exhibited by those elements. Chlorine and bromine, therefore, especially the former, almost always drive iodine out of iodides.

§ 208. The test for iodine is very characteristic. The free element combines with starch, forming a blue colour. A very small quantity of iodine may be thus detected. If the iodine is in combination, it is first liberated by the addition of a little chlorine. Iodine also forms an insoluble compound with silver (the iodide of silver, AgI), if a soluble iodide is mixed with a soluble salt of silver. The iodide of silver is of a light yellow colour; it differs from the bromide and chloride of silver on account of its much less solubility in ammonia. It is decomposed on boiling with strong nitric acid.

Combinations of Iodine with Oxygen.

There are two chief oxides of iodine, both of which form acids:—

Anhydrous iodic acid, I_2O_5 (?),	Hydrated iodic acid, HIO_3,
Anhydrous periodic acid, I_2O_7,	Hydrated periodic acid, HIO_4.

§ 209. *Iodic acid*, HIO_3.—Iodic acid may be formed by boiling iodine with nitric acid. The iodine is thereby slowly oxidized to iodic acid, while the nitric acid is deoxidized, and escapes as gaseous lower oxides of nitrogen. On evaporating the solution the iodic acid crystallizes out. When required in large quantity, iodic acid is usually prepared by boiling iodine with a solution of chlorate of potassium and a very little nitric acid. The reactions may be best described by the following equations:—

$$\begin{array}{rlll} (1) & HNO_3 + KClO_3 & = KNO_3 + HClO_3, \\ (2) & HClO_3 + I & = HIO_3 + Cl, \\ (3) & HIO_3 + KClO_3 & = KIO_3 + HClO_3, \\ (2) \text{ or } (4) & HClO_3 + I & = HIO_3 + Cl, \\ & \quad \&c. & \quad \&c. \end{array}$$

The small quantity of nitric acid liberates a corresponding quantity of chloric acid (equation 1), which oxidizes some iodine to iodic acid, and gives up its chlorine (equation 2). The so-formed iodic acid reacts upon a fresh quantity of chlorate of potassium, forming iodate of potassium and liberating a fresh quantity of chloric acid (equation 3), and so on. The small quantity of nitric acid is only necessary at first to start the reaction, and it afterwards remains inactive as nitrate of potassium. The result is that all the chlorine of the $KClO_3$ escapes as gas, and the iodine takes its place, being converted into KIO_3.

The iodate of potassium is then dissolved in water and mixed with chloride of barium, whereupon a difficultly soluble iodate of barium is formed.

$$2KIO_3 + BaCl_2 = 2KCl + Ba2IO_3.$$

The $Ba2IO_3$ separated from the soluble KCl is dissolved in boiling water and decomposed by the addition of exactly an equivalent of H_2SO_4. The result is that

$$Ba2IO_3 + H_2SO_4 = BaSO_4 + 2HIO_3.$$

$BaSO_4$, an insoluble salt, is formed, together with HIO_3. On filtering and evaporating the filtrate, the iodic acid, HIO_3, is obtained. Iodic acid has not been got in the anhydrous state. As prepared above, it is a white crystalline solid, freely soluble in water.

§ 210. *Periodic acid*, HIO_4.—Periodate of sodium, $NaIO_4$, is obtained by passing chlorine through a hot solution of a mixture of iodate of sodium and carbonate of sodium.

$$Na_2CO_3 + NaIO_3 + 2Cl = 2NaCl + CO_2 + NaIO_4.$$

On cooling, the periodate of sodium crystallizes out. This being dissolved in HNO_3 and treated with $AgNO_3$,

$$NaIO_4 + AgNO_3 = AgIO_4 + NaNO_3,$$

periodate of silver is formed, and, being difficultly soluble, is precipitated. The $AgIO_4$ having been purified by crystallization from hot nitric acid, is treated with water, which decomposes it into a basic periodate and periodic acid, HIO_4.

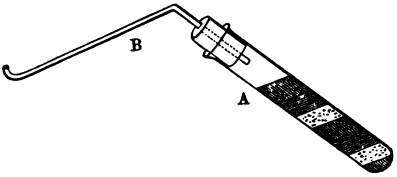
$$4AgIO_4 + H_2O = 2HIO_4 + Ag_4I_2O_9.$$

The basic periodate, $Ag_4I_2O_9$, being insoluble, is left; the periodic acid is got by filtration and evaporation. Periodic acid, HIO_4, melts at 130° C.; on being further heated, it loses water and is decomposed.

Combination of Iodine with Hydrogen.

§ 211. *Hydriodic acid*, HI, is formed in the same manner as hydrobromic acid. Like the latter body, and for the same reason, it cannot be formed by treating an iodide with sulphuric acid. Hydriodic acid, HI, is prepared by placing in a tube, A (fig. 63), alternate layers of iodine, phosphorus, and wet pounded glass. On gently warming the tube, the iodine and phosphorus unite, forming iodide of phosphorus (§ 275), which is immediately decomposed by the water into phosphorous and hydriodic acids,

Fig. 63.



$$PI_3 + 3H_2O = H_3PO_3 + 3HI,$$

the latter of which escapes through the tube B.

§ 212. Gaseous hydriodic acid is a colourless gas which fumes in moist air, owing to its meeting there with moisture with which it combines. It dissolves abundantly in water. It consists of equal volumes of hydrogen and of vapour of iodine, united without condensation; its density is therefore $\frac{127+1}{2}$ or 64 (compared with air 4·414). Hydriodic acid is easily decomposed, even by the oxygen of the air and by mercury, especially in bright light.

§ 213. The combinations of iodine with other of the preceding elements are of less importance. Iodine is not known in combination with carbon alone. It forms with nitrogen, or nitrogen and hydrogen, a solid black body, which, when dry, explodes on the slightest touch, and which is probably similar to the chloride of nitrogen (§ 198). The *iodide of nitrogen* is got by treating iodine with a solution of ammonia. A part or all of the hydrogen is thereby forthwith removed and replaced by iodine.

$$NH_3 + 6I = NI_3 + 3HI, \text{ or}$$
$$NH_3 + 4I = NHI_2 + 2HI.$$

Two *chlorides of iodine* are known. If chlorine be passed over iodine, the iodine melts, and is converted into a brown liquid consisting of ICl, which dissolves in water. The same body is formed when dry iodine and chlorate of potassium are heated in a retort.

$$KClO_3 + 2I = KIO_3 + ICl.$$

If excess of chlorine be passed over iodine or protochloride of iodine, the latter is converted into the terchloride of iodine, ICl_3, a bright orange-yellow solid body, soluble in water.

Comparison between Chlorine, Bromine, and Iodine.

§ 214. These three elements form a well-defined group, no less remarkable for the dissimilarity of its members to other elements than for the manner in which they resemble and differ from one another. They all unite directly with metals, and form neutral salts, hence they are sometimes called *halogens.* They are always found together in nature. They all form more or less insoluble salts with lead, mercury, and silver, and with no other metals. They are similar and peculiar in smell; they are soluble in the same media; they combine with almost all the other elements in the same numerical proportions. In fine, if any compound containing any one of the three is known, we may look with almost perfect assurance for the existence or discovery of similar compounds containing each of the others.

They differ from one another chemically more in *degree* than in *kind*; and bromine is, so to speak, the chemical mean between chlorine and iodine. Thus, iodine being a solid and chlorine a gas, bromine is a liquid, and the equivalent of bromine is nearly exactly half the sum of the equivalents of chlorine and iodine.

$$\begin{array}{rl} Cl = & 35{\cdot}5 \\ I = & \underline{127\phantom{{\cdot}5}} \\ 2) & \underline{162{\cdot}5} \\ & 81{\cdot}25 \qquad \text{Bromine} = 80. \end{array}$$

If the chloride of a metal is more soluble in water or any other medium than the bromide, then the bromide is more soluble than the iodide, and *vice versâ.* Chlorine expels bromine and iodine from combination with metals; bromine expels iodine, &c.

The body which most closely resembles the halogens is the compound body cyanogen, CN (see §§ 173 *et seq.*), and, in some respects, fluorine.

CHAPTER XI.

FLUORINE AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, Fl. *Equivalent,* 19. *Density,* 19 (compared with air 1·310).

§ 215. Fluorine is not well known in the separate state, on account of the energy with which it combines with other elements. It is believed to be a permanent gas of yellowish-green colour. Fluorine occurs in nature chiefly combined with calcium—as fluor-spar or Derbyshire spar, which is fluoride of calcium, $CaFl_2$. It is also found in small quantities in some other rocks (such as cryolite), in bones, and especially in the enamel of teeth.

Combination of Fluorine with Oxygen.

§ 216. No oxides of fluorine are known.

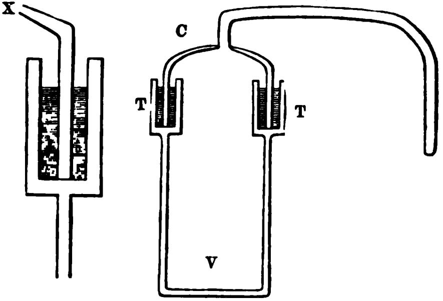
Combination of Fluorine with Hydrogen.

§ 217. *Fluoride of hydrogen,* HFl, or *hydrofluoric acid,* is obtained from fluoride of calcium on treating it with sulphuric acid.

$$CaFl_2 + H_2SO_4 = CaSO_4 + 2HFl.$$

Owing to the affinity of fluorine for silicon, which exists in all glass, porcelain, &c., vessels of these substances cannot be used for the preparation of hydrofluoric acid. The acid is generally made in vessels of lead, upon which metal hydrofluoric acid has little action. Fig. 64 shows a convenient arrangement. The vessel V is a cylinder of lead closed at the bottom. Its upper edge, T, is double, so as to form a trough running round the vessel. Into this circular trough fits the edge of the leaden cap C, bearing the leaden tube P. In V powdered fluor-spar and strong sulphuric acid are placed and mixed. The cap C is put in its place, and the trough T filled with sulphuric acid. X shows the arrangement of the trough and edge of the cap. On warming V, hydrofluoric acid escapes by the tube P, and may be condensed in the nearly anhydrous state, or absorbed by water held in a platinum, silver, or gutta-percha vessel at the extremity of P. To obtain the acid in the perfectly anhydrous state, it is distilled in a platinum retort from anhydrous phosphoric acid, P_2O_5.

Fig. 64.



§ 218. Anhydrous HFl is a colourless liquid, having the density of 1·3, and boiling at 30° C. It fumes in the air, and mixes with water in all proportions, combining with that body with great violence.

§ 219. Hydrofluoric acid and fluorides are detected by the power which the free acid has of attacking glass and other silicates. This is owing to the affinity of the fluorine for the silicon of such bodies. The substance under examination is powdered and warmed in a platinum vessel with strong sulphuric acid. There is held over the mouth of the vessel a plate of glass partly covered with wax. The liberated acid eats away or etches the exposed portion of the glass; so that when the wax is removed, those parts of the glass are found to be dull. The action may be represented thus:—

$$SiO_2 + 4HFl = SiFl_4 + 2H_2O.$$

The tetrafluoride of silicon being a gas, escapes from the surface of the glass as it is formed thereon (see Silicon, §§ 291–294).

§ 220. The fluorides of Mg, Ca, Ba, and Pb are insoluble in water. Solutions of these metals accordingly give precipitates with solutions of soluble fluorides, including hydrofluoric acid and fluoride of silver, which is soluble.

Compounds of fluorine with other preceding elements need not be described.

CHAPTER XII.

SULPHUR AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, S. *Equivalent*, 32. *Density of vapour*, 32 (compared with air 2·207).

§ 221. Sulphur in the free or uncombined state is found in the neighbourhood of volcanoes. It is chiefly obtained from Sicily and South America. In combination with metals it forms sulphides, many of which are found in nature, forming minerals often employed for the extraction of the metals which they contain. Such metallic sulphides are,

Iron pyrites......	sulphide of iron.
Copper pyrites....	sulphide of copper.
Galena..........	sulphide of lead.
Zinc blende......	sulphide of zinc, &c.

In combination with oxygen, and forming therewith an acid, sulphuric acid, it is found united with bases in rocks, as sulphate of calcium (plaster of Paris, gypsum, or selenite). It also occurs abundantly in the sea, and in many mineral springs, as sulphate of magnesium. In plants it is frequently found combined with carbon &c., especially in the natural order of the Cruciferæ. Sulphur also forms an essential part of animals, being found in albumen, in the horny tissues, and in blood. It does not form an essential part of the air, but is often found in impure air, owing to the putrefaction of animal and vegetable matter containing it, also to the artificial burning of sulphurous coal.

§ 222. Sulphur is generally prepared from the native sulphur by submitting it to distillation in earthenware retorts, whereby the rocky impurities are left behind; the sulphur melts, boils, and condenses in the receiver. Before being used, it is generally subjected to another distillation from iron retorts. If the vapour of sulphur be allowed to enter a large cool room, the sulphur condenses and solidifies as a coarse semicrystalline powder called "flowers of sulphur." If the vapours are only sufficiently cooled to become liquid, and the liquid is subsequently cast in moulds, it is called stick sulphur or "brimstone." Sulphur is also extensively prepared by heating large heaps of copper pyrites partly exposed to the air; the sulphur collects in the liquid form in cavities made in the heaps, and is thence tapped off.

§ 223. Sulphur is capable of assuming different modifications or allotropic conditions. (α) Native sulphur, or such as has been crystallized from a solution in sulphide of carbon or sulphide of chlorine, has the density of 2·05; it is nearly transparent, and crystallizes in rhombic octahedra. (β) Common brimstone (that is, sulphur which has solidified from a state of fusion) has a density of 1·98, and crystallizes in prisms. (γ) When sulphur is heated it melts to an amber-coloured liquid; if it be further heated, it deepens in colour and thickens. On still applying heat (which becomes latent), it deepens further in colour and thickens until it becomes almost black and solid. At a still higher temperature it becomes again somewhat liquid. If it be now suddenly cooled by pouring it in a thin stream into cold water, it is found to be converted into an amber-coloured transparent elastic solid. The above are the three chief modifications of the element sulphur; they may be distinguished by the symbols S^α, S^β, S^γ respectively. If S^γ be repeatedly melted and cooled, its colour gradually deepens, owing to the formation of a fourth modification, S^δ. Still other modifications of sulphur have been described; but their existence is somewhat doubtful. All modifications may be converted into S^α or S^β; the forms S^β and S^γ change spontaneously into S^α.

Sulphur melts at 114° C. and boils at 440° C. At this temperature, and up to 482° C., it has the density of 96 (compared with air 6·62). At 1040° C. and above, its density is 32. The latter is the density of sulphur when, in chemical combination with gases, it forms gases. Sulphur is insoluble in water. It dissolves in alcohol, ether, bisulphide of carbon, &c.

Combinations of Sulphur with Oxygen.

There are seven oxides of sulphur, all of which form acids; we need only consider two of the most common, namely, sulphurous and sulphuric acids.

§ 224. *Sulphurous acid*, SO_2.—When sulphur is ignited in the air, it burns with a pale blue flame and gives off a well-known suffocating smell. The only product of its combustion is anhydrous sulphurous acid, SO_2. If pure oxygen be passed over sulphur heated till it burns, pure sulphurous acid alone is formed. It is, however, more convenient to form sulphurous acid by deoxidizing sulphuric acid. This is usually done by means of charcoal, or, when the gas is required quite pure, by means of copper. Copper turnings are heated in a flask with strong sulphuric acid. A part of the sulphuric acid is decomposed, giving oxygen to the copper and escaping as sulphurous acid. The so-formed oxide of copper unites with some of the undecomposed sulphuric acid, giving rise to sulphate of copper; thus:—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

§ 225. Binoxide of sulphur, sulphurous anhydride, or anhydrous sulphurous acid, is a colourless transparent gas of suffocating smell and nauseous taste. It dissolves very readily in water, 100 vols. of water dissolving 6880 vols. of gas at 0° C. It may be condensed into a colourless liquid, under the ordinary atmospheric pressure, at a temperature of —10° C.; at 15° C. it requires a pressure of 2 atmospheres for liquefaction. It solidifies at —76° C. Sulphurous acid consists of 1 vol. of vapour of sulphur weighing 32, united with two volumes of oxygen, each weighing 16, and contracted to 2 vols. The density of SO_2 is therefore $\frac{2 \times 16 + 32}{2} = 32$ (compared with air 2·207).

§ 226. A solution of sulphurous acid in water acts as a bleaching agent; and sulphurous acid gas, got by burning sulphur in the air, is largely employed as a bleaching agent for woollen, silk, and straw.

§ 227. Sulphurous acid combines with many metallic oxides, especially with those of potassium, sodium, calcium, &c., and forms sulphites. Such sulphites are very similar in properties to the corresponding carbonates. Thus, when the carbonate of a metal is soluble, the sulphite is also soluble, and *vice versâ*. Sulphurous acid expels carbonic acid from most carbonates, but is itself expelled by most other acids, as nitric, hydrochloric, &c. Sulphurous acid does not burn when heated in the air, and it quenches burning bodies. The general formula of a sulphite is MSO_3 as K_2SO_3. Sulphurous acid is recognized by its peculiar smell (that of burning brimstone). Like carbonic acid, it is absorbed by alkalies and forms an insoluble salt with lime. It is detected by treating the body which contains it with zinc, water, and sulphuric acid; the hydrogen to which these bodies give rise (§ 92) deoxidizes the sulphurous acid completely, and combines with its sulphur to form the sulphide of hydrogen (see § 236), a gas of offensive and peculiar smell, which blackens salts of lead, silver, copper, &c. The reaction is as follows:—

$$K_2SO_3 + 3Zn + 4H_2SO_4 = K_2SO_4 + 3ZnSO_4 + 3H_2O + H_2S.$$

§ 228. *Sulphuric acid, anhydrous,* SO_3.—When sulphurous acid and oxygen gases are passed together over red-hot platinum, the two unite and form a white solid body, SO_3, which is sulphuric anhydride or anhydrous sulphuric acid. The same body is produced if oxide of copper and oxide of chromium are substituted for platinum; but in neither case does the body which causes the union of the two gases itself undergo any permanent change. SO_3 is also formed when the bisulphate of sodium is strongly heated. When sulphate of iron (called green vitriol) is heated in retorts, a heavy oily body passes over; this body is a mixture of anhydrous sulphuric acid, SO_3, and the body next to be described, H_2SO_4 (oil of vitriol). On gently heating the mixture and cooling the receiver, the SO_3 passes over first and condenses as a snow-white solid. Anhydrous sulphuric acid has a very great affinity for water, combining with it with violence and forming the hydrated acid. For this reason it fumes in ordinary air, on account of its vapour uniting with the water therein. The mixture of the anhydrous and hydrated acids got by heating sulphate of iron is sometimes called "Nordhaüsen sulphuric acid," and is employed by the dyer for dissolving indigo.

§ 229. *Sulphuric acid*, H_2SO_4, called also "oil of vitriol," is a very important acid, and is manufactured on a large scale. Sulphuric acid is prepared by oxidizing sulphurous acid. Peroxide of nitrogen, NO_2, in the presence of water gives up one equivalent of oxygen to sulphurous acid, converting it to sulphuric acid, and being itself reduced to nitric oxide, NO; thus:—

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO \text{............} \quad (a)$$

Nitric oxide, NO, in the presence of the oxygen of the air is converted into peroxide of nitrogen, NO_2 (§ 127).

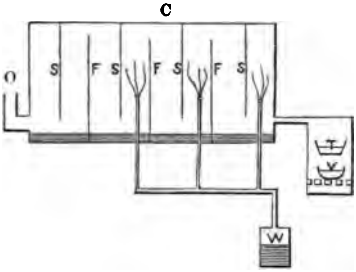
$$NO + O = NO_2 \text{.............................} \quad (b)$$

The peroxide of nitrogen is then again able to convert a fresh quantity of SO_2 into H_2SO_4, in the presence of water, according to equation (*a*). The result is that the same quantity of NO, by alternate oxidation to NO_2 and deoxidation to NO, serves gradually to convey an unlimited quantity of oxygen from the air to the sulphurous acid, thereby oxidizing an unlimited quantity of the latter.

§ 230. The arrangement adopted is in principle as follows:—A large chamber, C (fig. 65), lined with lead is provided with leaden screens hanging, S, S, S, from the ceiling, and rising, F, F, from the floor.

Entering this room at one end is the flue of a furnace, V. In V sulphur is burnt with an excess of air, and the heat of the burning sulphur acts upon a mixture of sulphuric acid and nitrate of soda contained in the vessel T. Water is boiled in the vessel W, and enters as steam into the chamber. The bottom of the chamber is covered with a thin layer of water. The action which takes place in V is

Fig. 65.



$$S + 2O = SO_2.$$

The action which takes place at T is

$$H_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2HNO_3.$$

Water arrives from W. These gases, SO_2, O, HNO_3, and H_2O, in passing round the screens become thoroughly mixed, and the following changes take place:—

$$\begin{aligned}
&(1)\ldots\ldots\ldots\ SO_2 + 2HNO_3 &&= H_2SO_4 + 2NO_2.\\
&(2)\ldots\ldots\ldots\ SO_2 + H_2O + NO_2 &&= H_2SO_4 + NO.\\
&(3)\ldots\ldots\ldots\ldots\ldots\ NO + O &&= NO_2.
\end{aligned}$$

The reaction of (1) is not repeated, but the reactions of (2) and (3) alternate with one another. The H_2SO_4 as it is formed is absorbed by the water on the bottom of C, and the excess of gas (atmospheric nitrogen) escapes by the opening at O. The acid is removed from the chamber and concentrated, first by boiling in glass vessels, and afterwards in platinum retorts; the excess of water is thus expelled.

§ 231. Sulphuric acid when pure is a colourless liquid of density 1·84. It boils at 325° C.

Sulphuric acid mixes in all proportions with water; in doing so, heat is evolved and the two contract to a volume less than the sum of the volumes of the constituents. This is owing to the formation of one or more definite hydrates of the acid. Sulphuric acid has indeed a great affinity for water. We have seen it used on this account for drying gases, which are made to bubble through it. For the same reason it is frequently used for drying bodies *in vacuo* at a low temperature. For if a wet substance be placed under the receiver of the air-pump and the air be withdrawn, the vapour of water will gradually fill the receiver, and the evaporation will cease unless the vacuum be renewed by continual pumping; but if a basin of sulphuric acid be also placed under the receiver, its surface will absorb the vapour of water, and the vacuum be thus definitely maintained. So great is the affinity of H_2SO_4 for water, that it often determines the formation of that body when in contact with substances which contain its elements. Thus sugar, wood, linen, &c. consist mainly (the first entirely) of carbon, oxygen, and hydrogen. On treating these bodies with H_2SO_4, the oxygen and hydrogen unite to form water which unite with the H_2SO_4; carbon is left; the body is blackened or charred; and the process is similar in its visible effect to the blackening of such bodies by heat.

§ 232. Sulphuric acid decomposes very many salts, and very often acts by combining with their bases and setting free the acids. Hence the great use of sulphuric acid in the arts for the manufacture of acids. We have already had examples of this.

$$CaCO_3 + H_2SO_4 = Ca\,SO_4 + H_2O + CO_2.$$

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

$$2KNO_3 + H_2SO_4 = K_2\,SO_4 + 2HNO_3.$$

§ 233. Sulphuric acid is also largely used in the manufacture of carbonate of sodium, for the formation of which sulphate of sodium is first prepared. The sulphate of sodium is got at the same time as hydrochloric acid by the action of H_2SO_4 upon NaCl.

§ 234. Sulphuric acid in the dilute form attacks many of the base metals, as zinc, iron, &c., liberating hydrogen and forming sulphates (see Hydrogen).

§ 235. Sulphuric acid and soluble sulphates are easily detected by the fact that sulphate of lead and sulphate of barium are insoluble in water and in acids. A liquid which is supposed to contain sulphuric acid, either free or as a soluble sulphate, is treated with a soluble salt of barium, as $BaCl_2$. If a precipitate is formed, and if that precipitate is insoluble in nitric acid, the original solution must have contained sulphuric acid; for though other salts of barium, as the sulphite, carbonate, phosphate, &c., are also insoluble in water, they dissolve in nitric acid.

Compounds of Sulphur with Hydrogen.

§ 236. *Sulphide of hydrogen,* H_2S, also often called *sulphuretted hydrogen, hydrosulphuric acid,* or *sulphydric acid.*—When organic matter containing sulphur rots or decomposes spontaneously in the presence of water, part of the sulphur often unites with hydrogen and escapes as a gas called sulphuretted hydrogen. This is the gas which gives the offensive smell to rotten eggs, cesspools, and the like. The same gas is formed at the mouths of many rivers, in consequence of the reduction of the sulphuric acid in the sulphate of magnesia of the sea by the carboniferous matter carried down by the stream.

§ 237. Hydrosulphuric acid, H_2S, is prepared in the pure state by decomposing a metallic sulphide by an acid containing hydrogen. Sulphide of iron, FeS, is formed by heating S and Fe together. This is broken into fragments and put in a bottle. Dilute sulphuric acid is poured upon it. Sulphate of iron is formed and sulphuretted hydrogen, H_2S.

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The sulphuretted hydrogen escapes as bubbles, and is collected by means of a tube passing through a cork in the neck of the bottle. So prepared, the H_2S generally contains a little H, owing to the presence of some Fe among the FeS. If the gas is required absolutely pure, the native tersulphide of antimony, Sb_2S_3, is gently heated with hydrochloric acid,

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S,$$

whereupon terchloride of antimony and sulphuretted hydrogen are formed.

§ 238. Sulphuretted hydrogen is a colourless gas of very offensive smell. Its composition by volume resembles that of water. 2 vols. of H, each weighing 1, unite with 1 vol. of S weighing 32; and the 3 vols. contract to 2. The density of the gas is therefore $\frac{2\times1+32}{2}=17$ (compared with air 1·17). Sulphide of hydrogen at ordinary temperatures becomes liquid when compressed with a force of about 17 atmospheres. At a temperature of $-85°$ C. it becomes solid. 100 vols. of water at ordinary temperatures dissolves between 200 and 400 vols. of this gas.

§ 239. When heated red-hot in the air, sulphuretted hydrogen burns with a blue flame, the products being sulphurous acid and water.

$$H_2S + 3O = H_2O + SO_2.$$

Sulphuretted hydrogen and sulphurous acid decompose one another in the presence of water,

$$5SO_2 + 5H_2S = 5S + 5H_2O + S_5O_5,$$

sulphur being separated, and a peculiar acid oxide of sulphur formed, called *pentathionic acid.* Sulphuretted hydrogen in the pure state acts as a violent poison, and even when largely diluted with air it is very injurious.

§ 240. The presence of sulphuretted hydrogen is easily detected by the ease with which the gas gives up its sulphur to metals in solution, forming with them sulphides. To detect the free gas, a strip of paper moistened with a solution of lead or copper is plunged into the gas, whereupon, if H_2S be present, PbS or CuS is formed; the paper in consequence becomes blackened, because the sulphides of these metals are black. The tarnishing of silver, especially in the air of towns, the blackening of the whites of oil paintings, and of most white paint, the blackening of silver spoons used for eggs or mustard, is due to the formation in each case of a black metallic sulphide.

§ 241. Sulphuretted hydrogen is continually used in the laboratory for separating and distinguishing metals in solution. The sulphides of some metals are soluble in water (K, Na, NH_4, Ca, Ba, &c.), others in dilute acids (Fe, Zn, Mn, &c.)*, others in alkalies (As, Sb, Sn, Au, &c). Hence, on passing a current of the gas H_2S through a solution of a mixture of metals, some will be precipitated as insoluble sulphides in neutral or alkaline, some in acid solutions, &c. Also the colours of the various metallic sulphides are often characteristic. Thus the sulphides of iron, nickel, lead, copper, &c. are black, those of cadmium and arsenic are yellow, that of antimony is orange, that of zinc is white.

§ 242. *Persulphide of hydrogen*, HS (?).—The composition of this body is doubtful, but it probably corresponds to HO (§ 109). It is prepared by adding CaS_2 to dilute HCl. The liquid, HS, collects as heavy oily drops insoluble in water, and which soon decompose into S and H_2S ($CaS_2 + 2HCl = CaCl_2 + 2HS$; and $2HS = S + H_2S$).

Compound of Sulphur with Carbon.

§ 243. *Bisulphide of carbon*, CS_2.—The only known sulphide of carbon is the bisulphide. This body does not occur in nature, but is manufactured on a large scale, being used for the solution of P and S, and of many natural hydrocarbons.

§ 244. CS_2 is prepared by heating charcoal to a bright redness in an earthenware retort or tube, and introducing fragments of sulphur. At that high temperature the two elements combine. The product, CS_2, passes over as a vapour, and is condensed as a liquid in the receiver, which must be well cooled.

---

* The sulphides in these cases are decomposed.

§ 245. Bisulphide of carbon, CS_2, is a transparent colourless liquid of disagreeable smell; it is heavier than, and immiscible with water. It dissolves in alcohol, ether, oil of turpentine, &c. It refracts light strongly, and is used to fill hollow glass prisms for optical purposes. It boils at 48° C., and has a density of 1·29. It burns when heated in the air, giving rise to carbonic and sulphurous acids.

$$CS_2 + 6O = CO_2 + 2SO_2.$$

In the state of vapour it consists of 1 vol. of C weighing 12, and 2 vols. of S, weighing each 32, the 3 vols. being condensed to 2 vols. The density of its vapour is therefore $\frac{12+64}{2}$ or 38 (compared to air 2·62).

Compounds of Sulphur with Chlorine, Bromine, and Iodine.

§ 246. *The sulphide of chlorine*, ClS, also called the *dichloride of sulphur*, is produced when dry chlorine is passed over melted sulphur in a retort. The sulphide of chlorine, ClS, collects in the receiver as a straw-coloured liquid. It is freed from excess of sulphur by distillation. Sulphide of chlorine boils at 138° C. It has a density of 1·687. It sinks through water, being insoluble, but is gradually decomposed by that liquid. It fumes in moist air, on account of the formation of HCl.

§ 247. *Protosulphide of chlorine*, Cl_2S, also called the chloride of sulphur, is obtained as a garnet-red liquid on saturating the bisulphide, ClS_2, with chlorine.

§ 248. Similar compounds of sulphur with bromine and iodine rae also known. IS_2 is a solid body.

Compounds of Sulphur with Nitrogen.

§ 249. *Sulphide of nitrogen*, NS, which possibly also contains hydrogen, is one of the many bodies which are formed when dry NH_3 is passed into ClS, dissolved in CS_2. It is a yellow crystalline body, which detonates when struck or heated to 155° C.

§ 250. *Sulphide of ammonium.*—There are several bodies consisting of sulphur, nitrogen, and hydrogen. The most important, from its constant use as a reagent, is NH_4HS, which is the sulphide of hydrogen and ammonium. It is got in the solid form, on mixing dry ammonia, NH_3, with dry H_2S.

$$NH_3 + H_2S = NH_4HS.$$

In solution it is obtained by passing H_2S into a solution of NH_3 in water. Besides this body, there are also known $(NH_4)_2S$ and $(NH_4)_2S_5$, the sulphide and pentasulphides of ammonium respectively.

§ 251. *Gunpowder.*—Though not a chemical compound, gunpowder may, on account of its importance, be here briefly described. It consists of an intimate mixture of nitrate of potassium (nitre, saltpetre), sulphur, and carbon (charcoal). When a certain amount of heat is applied to the mixture, a recomposition or rearrangement of the elements takes place. Some of the products of the recomposition are gaseous, and the formation and liberation of the gaseous products is necessarily attended by an effort to expand, which constitutes the bursting or propulsive force of the ignited powder. The gases formed are further expanded by the heat which accompanies the chemical change; and the effect of the powder is thereby largely increased.

§ 252. The three constituents are mixed in such proportion that the carbon is burnt, at the expense of the oxygen of the nitrate of potassium, to carbonic oxide and carbonic acid. The nitrogen is liberated, and the sulphur unites with the potassium. The products produced, however, vary with the pressure to which the exploding powder is subjected. And the proportions employed depend upon the degree of purity of the constituents used. Thus, the charcoal of different woods contains varying amounts of carbon.

English gunpowder contains usually about—

Nitre	75
Charcoal	15
Sulphur	10
	100

Prussian and French gunpowder contain the same percentage of nitre as the English; but the proportions of sulphur and charcoal in them are more nearly equal.

CHAPTER XIII.

PHOSPHORUS AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, P. *Equivalent*, 31. *Density of vapour*, 62 (compared with air 4·28).

§ 253. Phosphorus occurs in nature only in combination with other elements—indeed, almost invariably in union with oxygen (with which it forms a powerful acid), in combination with bases. In the primary or lowest, and in recent igneous rocks, as lava, it is found as phosphates of K, Na, Ca, &c. The quantity, however, of P is very small in rocks. Phosphorus occurs in plants, especially in such seeds as are used for food. It forms an essential constituent of bones, the ash of which consists almost wholly of carbonate and phosphate of calcium. Phosphorus is also found in the flesh, blood, brain, and excrements, both liquid and solid, of animals; hence, in part, the use of the latter as manures.

§ 254. Phosphorus, which is very largely employed in the manufacture of lucifer matches, is generally manufactured from the ashes of bones as follows:—The bone-ash, consisting of carbonate and phosphate of calcium, is treated with dilute sulphuric acid in excess, whereby sulphate of calcium is formed, carbonic acid escapes as a gas, and the phosphoric acid remains in solution along with sulphuric acid and lime, forming the so-called superphosphate of lime. The superphosphate is separated by decantation from the insoluble sulphate of calcium, and evaporated nearly to dryness with powdered charcoal. The mass so obtained is placed in earthenware retorts and submitted to a very high temperature. The carbon combines with the oxygen of the phosphoric acid, forming carbonic oxide, which escapes as a gas, whereupon the liberated phosphorus distils over and is collected under water, into which the neck of the retort dips. It is then remelted under water and purified by being forced by pressure through the pores of a leathern bag. It is afterwards usually cast into cylindrical sticks, in which form it occurs in commerce.

§ 255. Freshly made phosphorus is an almost colourless, slightly yellow, transparent solid of waxy consistence. Its density is 1·9; it melts at 44° C., and boils at 290° C. It may be distilled in a current of CO_2, H, or N. Exposed to the air, phosphorus gradually oxidizes, gives rise to a faint bluish light (called phosphorescent) and a peculiar smell (ozone, § 83). Heated to 60° C. by friction or otherwise, it enters into rapid oxidation or takes fire, burning with intense light and giving off white clouds of phosphoric acid. Phosphorus is insoluble in water, but soluble in alcohol, ether, &c., and especially in bisulphide of carbon. When kept, as it always is, under water, it gradually gets coated with a white skin of unknown composition.

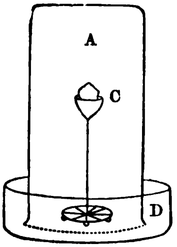
§ 256. When heated for several hours nearly to its boiling-point in some gas which does not act upon it, phosphorus undergoes a peculiar change in colour, in physical properties, and chemical energy. It becomes red, insoluble in bisulphide of carbon, much less fusible and oxidizable, and altogether less energetic chemically. This red phosphorus is often called amorphous phosphorus, and bears the symbol P^{β}. It is prepared by heating P for some hours to about 240° C. in a closed vessel, allowing the mass to cool, and washing it with CS_2, which removes the unchanged P. So got it forms a vermilion-red powder. If kept for several days at a temperature of about 230°, it is changed into a brittle solid mass. P^{β} is infusible; but when heated to 260° C. it is reconverted into ordinary P, and takes fire if exposed to O.

§ 257. Lucifer matches are usually made by first dipping the ends of the wooden splinters into melted sulphur, and then into a paste made of water, gum, nitrate and chlorate of potassium, oxide of lead or of manganese, and phosphorus—the whole being so rubbed up together that the phosphorus is in a fine state of division. When the matches are dry and are rubbed, the small particles of phosphorus begin to burn, the heat so developed liberates oxygen from the nitrate and chlorate of potassium and the metallic oxides. The increased supply of O so obtained assists the combustion of the rest of the P; and the result is the development of a heat sufficient to ignite the S, and thence the wood.

Combinations of Phosphorus with Oxygen.

§ 258. *Phosphoric acid, anhydrous,* P_2O_5.—When phosphorus is heated in dry air or oxygen (§ 80) it takes fire, and burns, giving off white clouds. These clouds consist of anhydrous phosphoric acid, P_2O_5. Fig. 66 shows the usual arrangement for making a small quantity of this body. A is a dry glass inverted into a dry dish D, and covering a little cup C, in which a fragment of P is burning. After some time the P_2O_5 is found condensed upon the sides of the glass and on the dish as a snow-white flaky deposit, and may be thence collected. Anhydrous phosphoric acid has a great affinity for water; it hisses when thrown into that liquid, on account of the heat developed by their union. This property of P_2O_5 is made use of to remove the last traces of water from many liquids and gases—the liquid being shaken with the anhydrous acid, or the gas passed over it. P_2O_5 volatilizes at a temperature below redness.

Fig. 66.



§ 259. *Hydrated phosphoric acid,* HPO_3, may be got by dissolving the anhydrous acid in water, evaporating to a syrup, and heating to a red heat in a platinum vessel. On cooling, a brittle glassy solid is obtained, called glacial phosphoric acid, or

$$H_2O + P_2O_5 = 2(HPO_3),$$

and containing one equivalent of water. The same body is more readily got by digesting P in a retort with somewhat diluted HNO_3. The HNO_3 parts with O to the P; when all the P has dissolved, the contents of the retort are distilled until the excess of HNO_3 has been expelled; the excess of water is driven off in a platinum vessel.

§ 260. On exposing HPO_3 to the action of a quantity of water exactly equal to that already in the acid, crystals of $H_4P_2O_7$ are got. Thus:—

$$2HPO_3 + H_2O = H_4P_2O_7.$$

If double the quantity of water is used, crystals of H_3PO_4 are formed. Hence there are three hydrates of phosphoric acid, the mono-, ter-, and tetrahydrate. Of these, the terhydrate is the most stable. On boiling either HPO_3 or $H_4P_2O_7$ for some time with water, they are converted into H_3PO_4. Corresponding to each of these acids there are three series of salts—monobasic, tribasic, and tetrabasic. The monobasic phosphates are generally called metaphosphates, the tetrabasic are called pyrophosphates, and the tribasic are the common phosphates. Thus, if M be any metal, we may have

MPO_3 = metaphosphate of M,
$M_4P_2O_7$ = pyrophosphate of M,
M_3PO_4 = (common) phosphate of M.

Or, again, either a pyro- or common phosphate may contain different bases, thus:—

M_2NPO_4 = phosphate of M and N,
$M_2N_2P_2O_7$ = pyrophosphate of M and N.

And common phosphate of sodium is tribasic phosphate of sodium and hydrogen.

Na_2HPO_4 = phosphate of sodium.
$Mg_2NH_4PO_4$ = phosphate of magnesium and ammonium.

§ 261. Tribasic phosphoric acid and the common phosphates are recognized by giving a yellow phosphate of silver when mixed with soluble silver-salts. Phosphates of calcium, barium, magnesium, lead, &c. are also insoluble in water; but all phosphates are soluble in nitric acid.

§ 262. *Phosphorous acid, anhydrous*, P_2O_3, is got by burning P in a limited quantity of dry air. It appears as a white volatile solid, miscible with water.

§ 263. *Phosphorous acid, hydrated,* H_3PO_3, is obtained by exposing P for a long time to moist air. The P gradually oxidizes, and the H_3PO_3 may be collected in a suitable apparatus. H_3PO_3 may be made more expeditiously and in a state of greater purity by decomposing the terchloride of phosphorus, PCl_3 (§ 268), by water. When these two bodies are brought into contact they decompose one another.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

On evaporation the HCl and excess of H_2O are expelled.

§ 264. *Hypophosphorous acid,* HO_2H_2P.—When P is boiled with oxide of calcium (lime) and water, the water is decomposed, a part of the P escapes as a gas in combination with H (§ 265), the rest combines with O to form hypophosphorous acid, which then unites with lime, forming hypophosphite of calcium.

$$3CaO + P_8 + 9H_2O = 3(Ca2(H_2O_2P)) + 2PH_3.$$

If baryta be substituted for lime, a corresponding barium-salt is obtained, $Ba2H_2O_2P$. From this compound the free acid may be got by treating with just enough sulphuric acid to precipitate all the barium as $BaSO_4$, and filtering from it. Hypophosphorous acid cannot exist either alone or in combination with bases without hydrogen; hence its formula is written HH_2OPO or HO_2H_2P.

Combinations of Phosphorus with Hydrogen.

Three hydrides of phosphorus are known, P_2H, PH_2, and PH_3. The first is a solid, the second a liquid, the latter a gas. We shall only consider the latter.

§ 265. *Phosphoretted hydrogen,* PH_3.—This gas, which has some similarity to ammonia, may be looked on as ammonia in which the N has been replaced by P. We have (§ 264) seen it formed when H_2O, CaO, and P are boiled together. It is made by heating in a flask, filled nearly full, hydrate of potassium, water, and phosphorus.

$$3KHO + 3H_2O + 4P = 3KH_2O_2P + PH_3.$$

The neck of the flask is furnished with a gas-delivery-tube, the end of which dips under water. When so prepared, phosphoretted hydrogen takes fire spontaneously as the bubbles of it, having ascended through the water, come into contact with the air. This remarkable property is due to the presence in the gas of a small quantity of the liquid phosphide of hydrogen, H_2P. The vapour of this liquid is spontaneously inflammable, and its combustion sets fire to the H_3P, which then burns to H_2O and P_2O_5. Thus,

$$2PH_3 + 8O = P_2O_5 + 3H_2O.$$

If a little alcohol be added to the contents of the flask, the liquid PH_2 is retained, and the PH_3 loses the property of taking fire in contact with the air. It may, however, always be ignited by contact with a burning body.

Phosphoretted hydrogen is also formed when phosphorous acid is heated.

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

Phosphoretted hydrogen is produced in nature when animal matter containing P rots or putrefies. The smell of foul fish is partly due to this gas; and the light which is emitted by such substances is owing to the gradual oxidation of the gas in the air. *Ignes fatui,* "Will-o'-the-wisp," &c. are supposed to be owing to the same cause.

§ 266. Phosphoretted hydrogen is a colourless gas, of an offensive smell, like that of stale fish. It consists of 1 vol. of P weighing 62, united with 6 vols. of H, each weighing 1, contracted to 4 vols.* Its density is therefore $\frac{62+6}{4}$ or 17 (compared with air 1·17). It is feebly alkaline, and may combine with HI to form the compound

$$PH_3HI \text{ or } PH_4I,$$

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* It is preferable to take the density of P as 62; at lower temperatures the specific gravity of P is lower. PH_3 may be supposed to consist of 1 vol. of P (=31) with 3 vols. of H (weighing each 1), contracted to 2 vols., being thus like NH_3. But, as a rule, the higher a vapour is heated the more nearly does its density approach that which it has in gaseous combination.

corresponding to NH_4I. On account of its similarity to ammonia in composition and properties, it is sometimes called *phospham.*

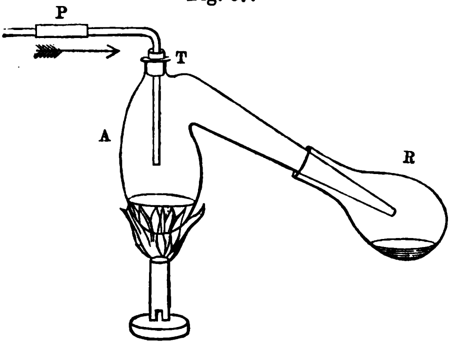
§ 267. *Carbide of phosphorus* is not at present known. *Nitride of phosphorus* is a body of doubtful composition; it is not known whether it contains hydrogen; it is at present of little interest.

Combinations of Phosphorus with Chlorine.

Two chlorides of phosphorus are known, PCl_3 and PCl_5.

§ 268. *Terchloride of phosphorus,* PCl_3.—Some dry sand is put into a retort, A (fig. 67), and upon this some pieces of dry phosphorus are laid. Through the cork in the tubulus T, a bent tube, P, passes and opens just above the phosphorus. Through this tube a current of perfectly dry chlorine (§ 181) is passed, while the retort is heated by a lamp. The two elements unite with flame, and the PCl_3 distils over into R.

Fig. 67.



§ 269. Terchloride of phosphorus, PCl_3, has a density of 1·45; its boiling-point is 78° C. 1 vol. of P (=62) combines with 6 vols. of Cl (each =35·5), and there is contraction to 4 vols.* The density of its vapour is therefore $\frac{62+6\times35{\cdot}5}{4}$ or 68·75 (compared with air 4·74). Thrown into water it at first sinks through, but is soon decomposed into H_3PO_3 and HCl.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

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* Compare note, p. 174.

We have already (§ 263) seen this reaction employed for making H_3PO_3. Owing to the mutual decomposition of PCl_3 and H_2O, the former fumes in moist air and gives rise to the acids H_3PO_3 and HCl, which irritate the eyes and lungs.

§ 270. *Pentachloride of phosphorus*, PCl_5, is formed by passing dry chlorine over PCl_3; the gas is immediately absorbed and a yellowish-white solid body is produced, which is the pentachloride of phosphorus. If the chlorine be used in excess, the PCl_5 is got quite pure.

§ 271. PCl_5 volatilizes without change at 148° C., and, unless under pressure, it does not previously fuse. Thrown into an excess of water the two bodies decompose one another with great violence, phosphoric and hydrochloric acids being produced, the former of which immediately combines with water.

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

§ 272. The density of the vapour of PCl_5 is derived as follows:—1 vol. of vapour of P (weighing 62) unites with 10 vols. of Cl (each weighing 35·5), and a condensation to 8 vols. follows. The density is therefore $\frac{62+10\times 35{\cdot}5}{8}$ or 52·12 (compared with air 3·59).

§ 273. *Oxychloride of phosphorus*, $POCl_3$.—When PCl_5 is exposed to moist air under a bell-jar, it is gradually converted into the oxychloride; that is, at first only two equivalents of Cl are extracted and replaced by one of O.

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

If PCl_5 be heated with the proper quantity of some body which parts with water with some difficulty, the same partial replacement takes place. It may for this purpose be heated with two equivalents of monohydrated oxalic acid (§ 160).

$$PCl_5 + H_2C_2O_4 = CO + CO_2 + POCl_3 + 2HCl.$$

$POCl_3$ boils at 110° C., and, like PCl_5, though not with so much violence, is decomposed by H_2O into H_3PO_4 and HCl.

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Combinations of Phosphorus with others of the preceding elements.

§ 274. The *terbromide* and *pentabromide* of phosphorus are similar in their formation and properties to the corresponding chlorine compounds; their formulæ are PBr_3 and PBr_5.

§ 275. There are two *iodides of phosphorus*, PI_2 and PI_3. Both are got by adding I in proper proportion to P dissolved in CS_2; on cooling they crystallize out as orange-coloured or deep-red solids.

§ 276. *Sulphides of phosphorus.*—Sulphur and phosphorus, when heated together under water, combine with explosive violence. Several such compounds are known, varying in composition according to the proportions of the elements employed, and so closely resembling one another physically, as to offer great difficulty in their separation. Such compounds may be made with less danger if red phosphorus is used; but a greater heat is then required to make the elements unite.

CHAPTER XIV.

SILICON OR SILICIUM AND ITS COMPOUNDS WITH THE PRECEDING ELEMENTS.

Symbol, Si. *Equivalent*, 28. (*Theoretical*) *density*, 56 (compared with air 3·86).

§ 277. Silicon, Si, occurs very abundantly in nature, but almost always in the form of oxide of silicon, SiO_2 (silicic acid), either alone or combined with bases, as Ca, Mg, K, Na, &c. In fact almost all rocks, with the exception of the carboniferous (limestone, dolomite, marble), consist essentially of silicates of the above metals. Silicic acid uncombined with any base constitutes quartz, flint, some kind of sea-sand, &c. In combination with aluminium it forms clay, slate, &c. In combination with aluminium and potassium it forms felspar. Granite consists partly of free silicic acid (or quartz), partly of silicate of aluminium and silicate of potassium (or felspar), and partly of silicate of aluminium and silicate of magnesium (or mica). The metals may vary, being replaced by others; but the silicic acid is an invariable constituent. Silicic acid is also found in plants, especially in the stalks of grasses, reeds, canes, &c., and in the husks of grain.

§ 278. Silicon, Si, may be obtained artificially by heating silicic acid with potassium; but it is prepared more advantageously by heating a double fluoride of silicon and potassium with sodium. The sodium withdraws the fluorine from the fluoride of silicon, leaving the potassium also in combination with fluorine. The fluorides of potassium and sodium are removed by being dissolved in water. The silicon is thereby left as a brown powder.

§ 279. Si^{γ}.—So prepared, silicon is heavier than water, and is not attacked by nitric or sulphuric acid. When strongly heated in the air, it burns with great brilliance, being oxidized to SiO_2. It may be fused under NaCl, and is got on cooling as a steel-grey mass harder than glass. Si^{γ} corresponds to the charcoal- or soot-form of carbon.

§ 280. Si^{β}.—Silicon may be got in a form similar to the graphitic form of carbon, and in a similar manner. On heating in a crucible the above-mentioned fluoride of potassium and silicon with Al, instead of Na, the Al withdraws the Fl, and the reduced Si dissolves in the excess of the melted Al. The latter metal is removed by treating the mixed mass with hot strong HCl, and traces of SiO_2 by means of HFl (§ 217). Silicon so obtained greatly resembles graphite, and is much less oxidizable than S^{γ}, the preceding modification of the element.

§ 281. Si^{α}.—Silicon may be obtained in a third modification—namely, the crystalline one, and corresponding therefore to the diamond or crystalline modification of carbon.* This form is got by passing the vapour of tetrachloride of silicon, $SiCl_4$ (§ 289), over metallic aluminium heated to a white heat in a porcelain tube. The aluminium withdraws the chlorine and forms a volatile sesquichloride of aluminium, Al_2Cl_6, the silicon being left as crystalline needles.

$$3SiCl_4 + 4Al = 2Al_2Cl_6 + 3Si.$$

Combination of Silicon with Oxygen.

Two oxides of silicon are known. We need only consider the binoxide or silicic acid.

§ 282. *Silicic acid, silica, or silex,* SiO_2, is found in an almost pure state as rock-crystal or quartz, which is a transparent crystalline form of the acid. Flint pebbles, flint sand, opal, chalcedony, &c. are more impure varieties. Combined with metallic oxides it forms most rocks (§ 277). To get the pure acid, such rocks are finely powdered and fused in a platinum crucible with Na_2CO_3. The cold mass is treated with dilute hydrochloric acid, evaporated gently to dryness, treated with strong hydrochloric acid, diluted with water, filtered, and washed. The action is this:—Some of the carbonate of sodium is decomposed by the silicic acid, silicate of sodium being formed and the carbonic acid expelled. The HCl decomposes the silicate of sodium and the excess of Na_2CO_3, setting free the CO_2 (which escapes as a gas) and the SiO_2. It further combines with any metallic oxides present, forming soluble chlorides. The second drying is to make all the SiO_2 perfectly insoluble in water. After washing and drying, the SiO_2 is obtained pure.

§ 283. Silicic acid so prepared is a light gritty white powder, insoluble in water and all acids, excepting hydrofluoric. It dissolves in hot strong solutions of hydrate of potassium. It combines with bases in an almost endless number of proportions, those silicates of the alkalies which contain the largest proportion of the alkali being the most soluble. Freshly precipitated SiO_2 is in combination with water, and is a gelatinous body soluble in hydrochloric acid. If such a solution be put into a porous vessel, as a vessel having an animal or vegetable membrane for a bottom, and be then surrounded by pure water, the HCl gradually leaves the SiO_3, passing through the membrane; the silicic acid is thus obtained as a solution in water.

§ 284. Anhydrous SiO_2 is harder than glass, and has a density of 2·6. The test for silicic acid and the manner of its estimation are based upon the reaction and process given in § 282 for its preparation. A more conclusive test will be given when we consider the compound of the element Si with Fl (§ 291).

§ 285. The uses of SiO_2 in the arts are very manifold. In the pure state, as quartz, it is used for optical glasses, lenses, prisms, &c. It forms many precious stones, as agate, carnelian, jasper, &c. As sand it is used to combine with lime and form mortar. Combined with alumina as clay, it forms the material for bricks, earthenware, porcelain, &c. Combined with Na, K, Ca, or Pb, it forms glass.

§ 286. As opal, SiO_2 is in combination with water. Definite hydrates may also be artificially obtained.

§ 287. *Hydride of silicon* has been obtained, but not in the free or unmixed state; its composition is not exactly determined.

§ 288. *Nitride of silicon* is got by saturating the tetrachloride, $SiCl_4$ (§ 289), with dry NH_3, and afterwards heating. The nitride is left as a white insoluble powder.

§ 289. *Tetrachloride of silicon*, $SiCl_4$, the only known chloride of silicon, is obtained by passing chlorine over an intimate mixture of carbon and silicic acid at a high temperature. Precipitated silicic acid is mixed with oil and powdered charcoal into a paste. This is then made into pellets and heated red-hot in a crucible, which is covered so as to prevent the burning of the carbon. The result is that the oil is decomposed, its carbon being left in intimate contact with the silica. The charred pellets are then placed in a porcelain tube, which is then heated white-hot, and a current of dry chlorine is passed through. The following decomposition takes place:—

$$SiO_2 + 2C + Cl_4 = SiCl_4 + 2CO.$$

The $SiCl_4$ is condensed in a well-cooled receiver, and appears as a colourless liquid of the density of 1·5, and which boils at 59° C.

The density of its vapour is derived thus:—1 vol. of vapour of silicon (theoretically weighing 28), united with 4 vols. of Cl (each weighing 35·5), condensed to 2 vols. The density is therefore $\frac{28+4\times 35{\cdot}5}{2}$ or 85 (compared with air 5·86). Terchloride of silicon is quickly decomposed by water into HCl and SiO_2.

$$SiCl_4 + 2H_2O = SiO_2 + 4HCl.$$

For this reason it fumes in moist air and has an acid smell.

§ 290. *Bromide of silicon*, $SiBr_4$, is similar in its preparation and properties to the chloride. The *iodide* is at present unknown.

§ 291. *Tetrafluoride of silicon*, $SiFl_4$, is the only known fluoride of silicon. It is obtained by treating silicic acid or a silicate with HFl.

$$SiO_2 + 4HFl = SiFl_4 + 2H_2O.$$

It may be got without previously making HFl, by treating silicic acid with a fluoride and H_2SO_4. For this purpose powdered fluorspar, sand, and sulphuric acid are gently warmed in a flask; the fluoride of silicon escapes as a gas.

$$SiO_2 + 2CaFl_2 + 2H_2SO_4 = 2CaSO_4 + SiFl_4 + 2H_2O.$$

§ 292. $SiFl_4$ is a transparent gas. It consists of 1 vol. silicon vapour (theoretical), weighing 28, united to 4 vols. of fluorine (theoretical), each weighing 19, condensed into 2 vols. Its density is therefore $\frac{28+4\times 19}{2}$ or 52 (compared with air 3·58).

§ 293. When passed into water this gas is immediately decomposed, silicic acid being formed and deposited, while a compound acid containing Si, Fl, and H, and called hydrofluosilicic acid, remains in solution in the water.

$$3SiFl_4 + 2H_2O = 2H_2SiFl_6 + SiO_2.$$

This reaction forms a means of preparing SiO_2 very readily, and in a state of the utmost purity.

§ 294. As we have already seen the formation of the tetrafluoride of silicon used as a test for fluorine (§ 219) by virtue of the power which HFl has of etching glass, so, inversely, silicic acid may be readily tested for by mixing the substance suspected to contain it with powdered fluor-spar and sulphuric acid, in a platinum vessel, and leading the gas formed into water. If silicic acid be present the volatile $SiFl_4$ will be formed, and this will be decomposed by the water, silicic acid being liberated.

CHAPTER XV.

COMBUSTION AND FLAME.

§ 295. When two bodies, either elements or compounds, in uniting with one another give rise to a great amount of heat, they are said to burn, and the process of their union is called combustion. The term combustion is often limited to the phenomenon of rapid oxidation or burning in the air. The oxygen is then said to be the supporter of combustion, and the burning body (that is, the body which visibly changes its condition or is consumed) is called the combustible. It is clear that this distinction arises from partiality of view, and that, since heat arises from the union of the two, each has the same title to the name combustible, and each to that of supporter of combustion. Further, the term combustion is usually limited to those extreme cases where the process of union is so energetic that light is produced.

§ 296. Every substance, solid, liquid, and gaseous, when heated to a certain temperature gives out light. Solids, as a rule, give out light at lower temperatures than liquids, and liquids at lower temperatures than gases. And at equally elevated temperatures solids give out more light than liquids, and liquids than gases.

§ 297. It often happens that the mere contact of bodies is sufficient to determine their rapid union and the evolution of heat and light. Thus chlorine and finely divided antimony, oxygen and finely divided lead, liquid hydride of phosphorus and air, &c. unite on mere contact, and evolve so much heat that they, or the products of their combustion, become red- or white-hot.

§ 298. It must be remembered that, whatever be the rate of union between two bodies, the total heat given out is the same, provided equal quantities of the same compounds are formed. Thus zinc, when gradually rusting in the air, gives out from first to last as much heat as when it rapidly oxidizes or burns. But in the former case, the heat, being developed slowly, escapes by radiation, convection, and conduction as fast as it is liberated, so that it is not perceived; in the latter case it is liberated in a short time, and part of it serves in the first place to heat the zinc or its oxide white- or red-hot. Whether the same quantity of light is given out in both cases is not known.

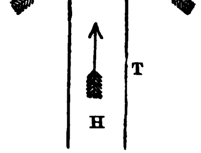
§ 299. In most cases of rapid union or combustion the heat is both a cause and a consequence of chemical change. Many bodies which do not burn rapidly at ordinary temperatures, burn completely when "set fire to." The obvious reason is this:—the two bodies in contact being heated at one of their places of contact, unite at that place; their act of union gives out heat, and this heat determines the union of the neighbouring particles with one another; so that the union or burning spreads with greater rapidity, according as the bodies are more intimately mixed, according as the heat evolved by their union is greater, and according as the temperature required for that union is less. Hence the apparently instantaneous union of hydrogen and oxygen, or of hydrogen and chlorine when the two gases are mixed and heat is applied to one part of the mixture. Hence, also, the use of finely grinding and mixing the constituents of gunpowder (§ 251)—carbon, sulphur, and nitre, so that each particle of the two former may be in contact with enough of the latter to receive oxygen (for the carbon) and potassium (for the sulphur) the moment a sufficient heat is reached.

§ 300. On the other hand, if one of the bodies which unites is in the solid or liquid form, and the other is a gas not miscible therewith, the extent of the surfaces in contact is limited, and union or burning can only take place more slowly. Thus, if a cup of melted sulphur be exposed to the air and just sufficiently heated to "take fire," the union of the two or burning of the sulphur only takes place at the surface of the melted sulphur, and proceeds slowly down as the SO_2 which is formed escapes and exposes a fresh surface to the air. Or red-hot carbon exposed to the air only burns at its surface, and the carbon is gradually "consumed" as the oxides of carbon formed escape. Further, a current of hydrogen entering the air through a tube may be "lit" at the end of the tube—that is, at the place where the O and H mix. The burning cannot pass back down the tube, because no oxygen is there; it cannot extend into the air, because no hydrogen is there.

§ 301. Flame may be defined as gas, vapour, or very finely divided solid matter, heated to such a temperature (in consequence of chemical change) as to give out light or become visible in the dark*.

§ 302. We may consider the case of H burning in O as a simple case of purely gaseous flame. Let (fig. 68) a current of hydrogen, H, as it issues from the tube T, be "set fire to." At C, or immediately above the tube, there is a cone of unmixed hydrogen; its lower part is cold, its higher part is hot owing to radiation from above. This cone, C, is greater according as the rate at which the H is delivered is greater. At B, and completely surrounding C, there is a conical sheath of flame; that is, B is the field where the union of the two gases is continually carried on. It is there that the water is formed; it is there that heat is liberated; and it is the intensely heated

Fig. 68.



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* In a few instances chemical decomposition gives rise to flame, as when chloride or iodide of nitrogen explode. This is probably due to the sudden compression of the neighbouring air, which we know to be a source of heat (Part I. § 12).

vapour of water there which in this case constitutes flame. The hottest part of B is of course that part where the H meets with exactly the proper quantity of O to form water. At the lower part, and towards C, there is an excess of H, at the higher part there is an excess of O. In both cases the excess of gas is heated by the combination of the rest. So that the flame B consists at its lower part of heated vapour of water mixed with H, at its middle of heated vapour of water alone, at its higher part of heated vapour of water and O. That there is little heat in the part C may be shown by introducing there the end of a match. The match does not take fire; on the contrary, if already burning, it is extinguished in consequence of want of O.

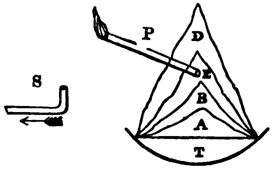
§ 303. When H burns in *air*, the N of the air which takes no part chemically in the process is, of course, also heated till it becomes luminous in the zone B. The N is found in all parts of the flame. The *shape* of the flame is due to the ascent of heated currents of vapour from the flame itself, and to the arrival of fresh air from around.

§ 304. Gases, even when intensely heated, give out but little light. Solid matter gives out light at lower temperatures; and the intensity of the light is increased by the temperature. When H burns in the air it gives out very little light, because the gases themselves, and the product of their union, are all gases. But if some solid body which is non-volatile, but which may be either combustible or incombustible, be brought into the flame, it becomes intensely heated, and gives off a great light. Thus if ZnO, MgO, CaO, or C be sprinkled in fine powder through the hydrogen-flame a brilliant light is produced, although in the first three cases no chemical change occurs, and although the heat remains the same. The same effect is produced by holding a piece of platinum wire in the flame. One of the brightest lights, the lime-light, is produced by introducing a piece of lime into the flame of the oxyhydrogen blowpipe (§ 101).

§ 305. In order, therefore, that a flame may give out a strong light, it is necessary that, by some means or other, there should be solid matter in it, heated to a high temperature. If such is not the case, little light is produced. The solid matter which gives light to flames is mostly derived from the body which burns, or is itself a product of that burning. This will become clear if we recall a few instances of combustion. Thus, when S, H, SH_2, or CO unite with O, scarcely any light is given out, because the products of oxidization are all gases, namely, SO_2, H_2O, SO_2+H_2O, and CO_2 respectively. Similarly, if S, H, or P unite with Cl, little light is produced, because SCl, HCl, and PCl_3 are all gases or vapours; but if P, Fe, or C unite rapidly with O, great light is produced, because P_2O_5 and Fe_3O_4 are solid bodies, the first nearly, and the second quite fixed; and in the case of the charcoal, a part of the fixed solid is heated to whiteness by the burning of another part.

§ 306. When a compound body is burnt in the air, the elements of which it is formed oxidize at different parts of the flame (supposing them all to be oxidizable), the one taking precedence of the other; and when an element has different stages of oxidation, different oxides will be formed in different parts of the flame. Thus, imagine (fig. 69) the spirits of turpentine, T, in a cup to be burnt. Spirits of turpentine has the composition $C_{10}H_{16}$. The heat of the applied match, and afterwards that of the burning turpentine, raises a part of the liquid as vapour; this is represented by A. The first quantity of oxygen which the vapour meets with burns only the hydrogen of the $C_{10}H_{16}$; water is formed and the C is set free. Being solid and greatly heated by the burning of the H, the very minute particles of C give out light. The conical shell B consists therefore of H_2O vapour and white-hot C, mixed with inactive N. This is the part of the flame which gives out most light, and is called the "luminous

Fig. 69.



zone." The white-hot carbon rising and meeting with more oxygen is first at E burnt to CO. Finally, as it rises, meeting with still more O, it is burnt to CO_2 at D. The water which is formed at B is carried up through E and D, and the nitrogen of the air exists in all parts of the flame, but of course not at A; so that we find—

Throughout A.—Vapour of turpentine.
„ B.—Formation of water, liberation of carbon, presence of nitrogen.
„ E.—Formation of carbonic oxide, presence of water and nitrogen.
„ D.—Formation of carbonic acid, presence of water and nitrogen.

That there is free carbon at B is at once shown by holding a cold body in that part of the flame; it becomes covered with soot or lampblack. That carbonic acid and water are the ultimate products is shown by holding a dry cold glass inverted over the flame. Its inside becomes covered with condensed water as a dew, and on shaking the collected gas with lime-water, insoluble carbonate of calcium is formed. That carbonic oxide occurs at E is shown by introducing a tube P open at both ends into that part of the flame; the gas which issues from the higher end may be lighted.

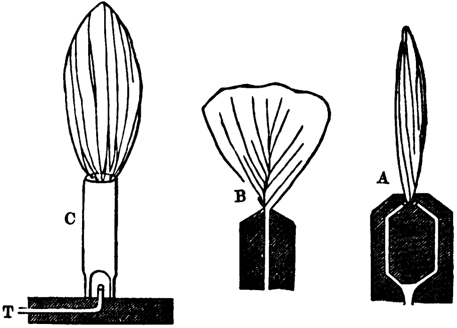
§ 307. If the supply of air is deficient, some of the carbon may escape oxidation altogether and issue unburnt from the upper part of the flame; the flame then becomes "smoky." If the supply of air is very abundant and rapid, the hydrogen and carbon are burnt at the same time (there is nowhere solid carbon); the flame loses its brilliancy.

§ 308. In order to get the greatest *lighting effect* out of a burning hydrocarbon, the supply of air must be so regulated that the hydrogen may be burnt first, so that the carbon may remain as long as possible in an "incandescent" state—that is, white-hot; at the same time there must be air enough to burn the carbon fully at last.

§ 309. In order to get the greatest *heating effect* out of a burning body, the supply of air must be more abundant, so that none of the heat of the burning hydrogen may be expended upon heating the carbon; but it must not be so abundant as to cool the flame by mere physical contact below the temperature of oxidation (blow it out).

§ 310. The difference made by the quantity of air supplied to a flame may be illustrated by two common gas-lamps—the "bat's wing" and the "Bunsen" burner. In the former, the holes out of which the gas issues are so opposed to one another as to throw the gas into a sheet, so that the illuminating surface is large and of such a size as to deliver, at the ordinary pressure at which the gas issues, just sufficient gas for its hydrogen to be burnt before the carbon (fig. 70). A shows the arrangement of the tubes and the appearance of the flame, seen edgewise. B shows the flat side of the flame; but one of the gas-tubes is hidden by the other. In the Bunsen burner C the gas enters by the tube T, and soon after entering the chimney C, it is mixed with air which enters through little arches at the bottom of the chimney. The gas burns at the top of the chimney, and being already mixed with sufficient oxygen to unite with the C and H, it gives out little light, but great heat*.

Fig. 70.



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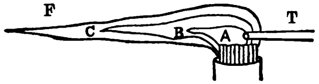
* It has lately been successfully shown that solid matter is by no means necessary for the production of great luminosity. When feebly luminous

§ 311. The blowpipe increases the intensity of heat by increasing the supply of air. If air (fig. 71) be forced through the tube T into the flame F of an oil-lamp, the flame becomes elongated and less luminous. It is then found to consist of three zones:—A is formed of injected air mixed with vapour of oil; B, where the hydrogen of the oil is burnt to water, and its carbon to carbonic oxide; C, where the carbonic oxide is burnt to carbonic acid, and where there is an excess of oxygen. Since there is an excess of carbonic oxide in B and an excess of oxygen in C, the first is called the *reducing*, the second the *oxidizing* flame of the blowpipe. The oxide of a metal may give up its oxygen to the hot carbonic oxide in B and be *reduced.* It may be again oxidized if placed at C in the hot oxygen which is there.

Fig. 71.



§ 312. Many substances used for illumination (such as tallow, wax, oil) contain oxygen, but never enough of it to form both water with the hydrogen and carbonic acid with the carbon, which are the other elements in the bodies. Others, such as coal-gas, contain the indifferent gas nitrogen. The contents of the different parts of the flame are of course modified by the presence of these gases; but the general structure remains the same in principle.

§ 313. If the burning body be not volatile without decomposition, the lowest cone, A (fig. 69), will consist of the vapours of

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flames are subjected to pressure their luminosity is increased. It appears that the light is greater according as the density of the heated gases and vapours is greater. It has been asserted that the soot or lampblack of luminous carbon-flames is indeed a compound of carbon with hydrogen, and exists in the flame in the form of a very dense vapour. It is undeniable that the brightest carbon-flame is transparent. These facts, however, in no manner militate against the received idea that solid matter in a flame increases its luminosity.

the substances into which the original body is separated by heat alone; such are called the products of its "destructive distillation." Thus, in the case of tallow, this cone contains marsh-gas, olefiant gas, and a great variety of other gases and vapours.

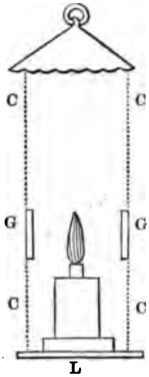
§ 314. If by contact with cold and good conducting bodies the gases concerned in a flame are cooled below a certain temperature, the combustion cannot continue and the flame is extinguished. Hence, if a piece of metal be held in the flame of a candle, it will be seen that the flame does not touch the metal, but is separated from it by an interval of perhaps $\frac{1}{40}$ of an inch. If the metal gets red-hot, as a pin may do, or if it gets covered with soot, which is a bad conductor of heat, the flame touches it again. It appears as if the flame were repelled; such is not the case, but the combustion in the neighbourhood of the cool body is arrested, and the gases there are cooled below the temperature of incandescence. Thus a candle may be put out by passing over its wick without touching it a metal ring of a little larger diameter.

§ 315. Again, a mixture of two gases which unite with violence when heated together, may produce a flame at one end of a tube through which it issues, and the flame (fig. 72) will not travel back through the tube, igniting the mixture as it goes, if the orifice of the tube is narrow. The edge of the tube cools the mixture below the temperature at which combination is possible.

Fig. 72.

§ 316. The miner's safety-lamp, or Davy's lamp, acts upon the same principle. It consists (fig. 73) of an ordinary small lamp, L, enclosed in a cylinder, C, of fine wire gauze. Opposite the flame, the cylinder is of glass, G. The firedamp or marsh-gas (§ 169) given out from the coal may get mixed with the air of the mine in such a proportion that, when a naked flame is brought into contact with it, the whole mixture explodes. When such a gauze-covered lamp is introduced into such an explosive mixture, the gas of course penetrates through the gauze and reaches the flame, where it is ignited. The explosive mixture burns in little jets of flame on the *inside* of the wire gauze, but cannot pass through, on account of the cooling action of the metallic wire.

Fig. 73.



§ 317. *Fuel*, or the matter whose rapid oxidation gives rise to heat used in the arts, may be solid, liquid, or gaseous. Almost all fuel which is employed in the arts is of vegetable origin. Wood, peat, turf, coal, charcoal, coke, coal-gas, turpentine, petroleum, naphtha, spirits of wine, and most kinds of oil are all derived from plants which have been subject to natural or artificial changes. A few, such as tallow, wax, spermaceti, and some oils are of animal origin. The mineral surface of the earth is very completely oxidized, witness the free oxygen of the air. Since oxidation is the process which takes place when fuel is burnt, it follows that there are no purely mineral fuels.

§ 318. But, as we shall see (Chapter XVI.), one of the functions of plants is to deoxidize the carbonic acid of the air and to store up the carbon in their tissues, in combination with less oxygen than it has in carbonic acid, generally with as much as it has in carbonic oxide. It is not known whether plants deoxidize water; but the growth of plants and the formation of their wood may be roughly described as the withdrawal, or rather rejection, of oxygen from carbonic acid and water, thus:—

$$\text{Wood} = \text{Carbonic acid} + \text{Water} - \text{Oxygen}.$$

§ 319. Wood contains and consists of other constituents (Si, P, N, S, and metals Ca, K, Na), got from the earth; these, which make but a small percentage of the wood, vary in kind and quantity; the above three, C, H, and O, are always present. In the purest form of woody fibre the three elements are present in the proportion

$$C_6H_{10}O_5;$$

that is, the O and H are in the same proportion as in water. Wood may be called a carbide of water.

§ 320. Wood when green, and generally unless artificially dried, contains a large quantity of moisture. When such wood is burnt, a part of the heat produced by the oxidation of carbon and hydrogen is expended in raising the temperature of this water to 100° C. (capacity for heat of water). A further portion is used for converting the water into steam (latent heat of steam). Consequently wet or damp wood on burning does not give out so much heat as it would do, and does, if first dried. Water or moisture in fuel, though it increases its bulk and weight, and may not be sensible to the touch, is therefore a disadvantage. A pound of damp wood, when burnt, gives out a certain quantity of heat. When dried, though it weighs less than a pound, it gives out on combustion more heat.

§ 321. *Coal.*—When wood is buried in the earth it gradually loses the elements of water; it darkens in colour, and approaches in composition to pure carbon. The longer it has been buried the more perfect is this change, and the longer the time of its burial and the greater the pressure to which it has been subjected, the more compact is its structure. It is to be remarked that woody fibre loses water even when in continual contact therewith, so that turf and peat, originally of nearly the same composition as wood, as they remain buried, even in bogs and wet places, lose water, and approach in composition to coal. *Lignite,* or brown coal, is wood which is imperfectly converted into coal; it still contains oxygen, and consequently, when burnt, does not give rise to so much heat as does the same weight of more perfect coal. The oldest coal is nearly pure carbon, with a little hydrogen; and the hydrogen gradually escapes, in combination with carbon, as marsh-gas or firedamp (§ 169).

§ 322. *Charcoal.*—When wood is rapidly heated, the air being excluded, the same changes go on as take place during the formation of coal, but more quickly. At first water is expelled, then in succession bodies containing carbon, hydrogen, and oxygen, that which remains behind becoming poorer in oxygen and hydrogen, until at last carbon is left as charcoal, which retains the original form of the wood. In charcoal the whole of the mineral constituents of the wood are retained, while in coal, in consequence of the percolation of water during its burial in the earth, the mineral constituents of the wood may be washed away, and in part replaced by others which the water held in solution.

§ 323. *Coke,* which may be defined as the charcoal of coal, is got by heating coal in close vessels, as in the manufacture of gas. Coke made from old coal is almost pure carbon. Most of the oxygen and mineral constituents have been removed during the conversion of wood into coal; and the hydrogen and remainder of the oxygen are expelled in combination with carbon as coal-gas, naphthaline, coal-tar, paraffin, naphtha, creosote, and many other compounds, or in combination with one another as water; while the small quantity of nitrogen is expelled, partly in the free state mixed with the coal-gas, partly in combination with hydrogen as ammonia.

§ 324. *Petroleum* is a mixture of hydrocarbons; it is also called "rock-oil," mineral naphtha, &c. It is formed by the action of the heat of the earth upon buried coal. It frequently oozes through the surface of the earth, and is collected from natural oil-springs or artificial wells.

§ 325. In order to get the greatest heating effect out of any fuel, it is of course necessary that the fuel should be fully burnt. Grates and furnaces are therefore to be so constructed, and their fires so stoked, that there shall be the least possible escape of smoke or unburnt carbon, and of carbonic oxide.

§ 326. The following Table shows the comparative heats given out when equal weights of certain elements burn in oxygen. It is supposed that such a weight of H is taken as gives 100 units of heat when oxidized to water; the same weights of the other elements are taken:—

grm.						
0·0290	of Hydrogen,	when burnt to	H_2O,	gives	100	units of heat
,,	Charcoal	,, ,,	CO_2	,,	23·5	,,
,,	Graphite	,, ,,	CO_2	,,	22·6	,,
,,	Diamond	,, ,,	CO_2	,,	22·5	,,

grm.							
0·0290 of	Phosphorus	when burnt	to	P_2O_5	gives	16·7	units of heat·
„	Sulphur	„	„	SO_2	„	6·4	„
„	Iron	„	„	Fe_3O_4	„	4·6	„
„	Zinc	„	„	ZnO	„	3·8	„

CHAPTER XVI.

THE ATMOSPHERE.

§ 327. The atmosphere is that part of the globe which is in a gaseous state. Since every gas is lighter than every liquid and every solid, it follows that the atmosphere forms the external coating of the earth. The attraction of the earth keeps the atmosphere in contact with the earth. Since all gases tend to mix with one another, the atmosphere contains in almost constant proportion all the permanent gases which are in it. Since the atmosphere has weight, and since the density of a gas varies directly as the pressure to which it is exposed, it follows that the lower or more earthward parts of the air are the more dense.

§ 328. Nothing is known with regard to the superior or external surface of the air. There is no conclusive evidence to prove that it has any limit whatever. But the higher we rise the less dense becomes the air, until its density becomes inappreciably small.

§ 329. Atmospheric air is 14·5 times as heavy as hydrogen. The pressure which the air exerts upon the surface of the earth at the sea-level is about, on an average, 15 lbs. to the square inch, and varies from about 14 lbs. to about 16 lbs. It supports a column of mercury 30 inches, or 760 millims. in height.

§ 330. the average composition of the atmosphere is as follows, by volume:—

Nitrogen..............	77·95
Oxygen	20·61
Carbonic acid	0·04
Vapour of water........	1·40
	100·00

The quantity of vapour of water in the air, however, is continually varying, and therefore influencing the whole amount of the other constituents, but without affecting their relative quantity. The proportion of N, O, and CO_2 varies very slightly in pure air. Collected at the tops of the loftiest mountains, during balloon-ascents, or at the sea-level, its composition is almost the same. There are generally in the air also traces of nitrous acid, ammonia, and marsh-gas. In towns, or crowded and ill ventilated rooms, the quantity of carbonic acid is greater.

§ 331. The composition of the atmosphere is maintained constant by the counteraction of numerous influences; these we must briefly examine. The flesh and tissues of animals are continually undergoing renovation; fresh matter is being carried to them through the arteries, and the waste, or no longer serviceable portion of them, is being carried away by the veins. It is carried to the lungs, and is there brought into contact with the inspired air, and becomes burnt or oxidized. Part of the products of this oxidation remain for a time in the blood and is got rid of by the kidneys; part is ejected at once in the breath. The waste compounds of carbon and hydrogen which are oxidized in the lungs to carbonic acid and water, escape as such in the expired breath. The well-known dampness of the breath is evidence of the water therein. If the breath be passed through lime-water, the lime is precipitated as carbonate of calcium, showing the presence of carbonic acid.

The air which is taken into the lungs on inspiration is found on expiration to be poorer in free oxygen, richer in carbonic acid and in watery vapour. Animal life is therefore a never-ending source of carbonic acid to the air. The immense quantities of wood, coal, gas, charcoal, coke, oil, fat, &c. burnt by man add a large amount of carbonic acid to the air. A very much larger quantity enters the air through the natural decay of wood, leaves, and other vegetable matter. Finally, a certain quantity is ejected from active volcanoes and mineral waters.

§ 332. This continual supply of carbonic acid is kept down by vegetation. Assisted by the light of the sun, the leaves of plants have the power of reducing or deoxidizing carbonic acid, rejecting oxygen, and storing up the reduced carbon in combination with water, as wood, starch, gum, &c., all of which consist of carbon and hydrogen united with as much oxygen as would form water with the hydrogen.

$$C_mH_{2n}O_n.$$

It is true that at night, when the action of the sun has ceased, the leaves of plants give off carbonic acid, which is the product of the oxidation of the waste woody fibre and vegetable tissue. But the plant, as long as it is growing, effects on the whole a continual removal of carbonic acid from the air, and a storing up of the carbon in a less oxidized state. As far as its carbon is concerned, a plant may be said to breathe twice only in the twenty-four hours—one inspiration extending from the rising to the setting of the sun, during which the plant absorbs and digests the carbonic acid of the air, one expiration extending from the setting to the rising of the sun, during which the plant gives up a certain quantity of carbonic acid.

§ 333. It accordingly follows that, *during the day*, the expired breath of animals serves as food for plants, and the expired breath of plants contains additional oxygen fit for animals to respire,—and that, *during the night*, plants and animals require the same constituents of the air, namely oxygen, and give rise to the same gas, carbonic acid. Hence the neighbourhood of plants is healthy for animals during the day, unhealthy during the night.

§ 334. Opinions are still divided as to whether plants may obtain their nitrogen directly from the free nitrogen of the air, whether they get it through the leaves from the small quantity of ammonia in the air, or whether it enters into the plant only through the roots, along with the metallic constituents required by the plant. The quantity of nitrogen in plants, however, is comparatively so small, that in any case the amount of nitrogen in the air cannot be appreciably affected by vegetable growth.

§ 335. The nitrous acid in the air, which may be detected in the first shower following a summer thunderstorm, is supposed to be due to the direct union by the electric discharge of the free atmospheric nitrogen and oxygen. It is probably also formed by the oxidation of the minute germs of certain plants, which are known to exist in all air, and which doubtless contain nitrogen.

§ 336. Ammonia is probably mainly due to the putrefaction of nitrogenous animal and vegetable matter; or it may be formed simultaneously with nitrous acid—by the electric decomposition of water, and the union of both of its elements with nitrogen.

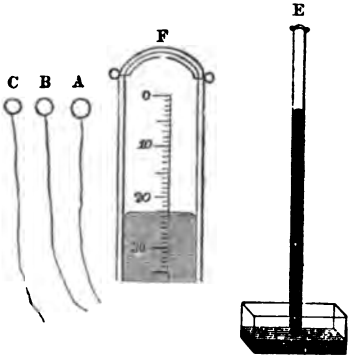
$$4H_2O + 4N = 2(NH_4NO_2).$$

§ 337. The air of English towns usually contains traces of sulphurous and sulphuric acids. This is owing to the presence of sulphur in the coal used as fuel, its oxidation to sulphurous acid in the fire of the furnace, and the further gradual oxidation to sulphuric acid in the air.

§ 338. The analysis of atmospheric air is very easily performed. To determine the quantity of moisture in it, a known volume is made to bubble slowly through a weighed quantity of strong sulphuric acid. The sulphuric acid absorbs all the water, but does not affect the carbonic acid, the oxygen, or the nitrogen. If the air so dried be made to bubble through a known weight of a solution of hydrate of potassium, the carbonic acid is absorbed; the oxygen and nitrogen pass through. If, finally, the mixed oxygen and nitrogen so deprived of water and carbonic acid be led over a weighed quantity of metallic copper heated to redness, the oxygen is absorbed, oxide of copper being formed. The increase in weight of the sulphuric acid gives the quantity of water; that of the hydrate of potassium gives the carbonic acid; that of the metallic copper gives the oxygen. The quantity of nitrogen is, of course, the difference between the weight of the quantity of air originally taken and the sum of the weights of the water, carbonic acid, and oxygen.

§ 339. The analysis of a small quantity of air is generally performed in what is called a "eudiometer," which is a long glass tube closed at one end, and graduated or marked in such a way that its contents from the closed end to any mark is accurately known. Two platinum wires are fused into the tube at the closed end so as nearly to touch one another in the inside of the tube (fig. 74). Such a tube is filled with

Fig. 74.



mercury, and a little air is allowed to bubble up, and is measured by seeing how far it depresses the mercury. A small fragment of coke, A, which has been moistened with sulphuric acid and deprived of air in a barometric vacuum is then pushed up (by means of a wire fastened to it) into the gas, and after a time withdrawn. The decrease of volume thus effected gives the volume of the aqueous vapour. Secondly, a pellet of solid hydrate of potassium, B, is similarly introduced and withdrawn; the resulting contraction gives the volume of carbonic acid. Finally, a pellet of phosphorus, C, is introduced in a similar manner and allowed to remain for some hours. The diminution thereby caused is the volume of oxygen. The oxygen may be also determined by introducing a measured excess of hydrogen, and passing an electric spark through the mixed gases by means of the platinum wires; the diminution thus caused is equal to the volume of oxygen. Account must be taken in such analyses of the varying pressure and temperature at which the several measurements are made.

CHAPTER XVII.

NATURAL WATERS.

§ 340. Although water in its pure state is a perfectly definite chemical compound, and has been considered as such in Chapter VI., yet the water which is met with in nature is never pure, but holds in solution various substances according to the nature of the bodies it has met with in its career.

§ 341. We may start from any one of the natural reservoirs of water, and trace the kind and degree of influence to which the water is subsequently subjected.

§ 342. The surface of the sea occupies about two-thirds of the surface of the globe; it extends in depth in places to about eight miles; its composition is nearly the same everywhere. The sea of the British Channel has the density 1·027; and its composition is as follows:—

Water	96·374
Chloride of sodium	2·806
,, potassium	0·077
,, magnesium	0·366
Bromide of magnesium	0·004
Sulphate of magnesium	0·229
,, calcium	0·141
Carbonate of calcium	0·003
	100·000

It contains, besides, inappreciably small quantities of iodine, ammonia, and iron, and doubtless all the other constituents of the earth in such small quantity as to escape detection. The most abundant constituents are accordingly the chlorides of sodium and magnesium, and the sulphates of magnesium and calcium.

§ 343. The accumulation of solid matter in the sea, owing to the large quantity of solid matter carried down to it by the rivers is counterbalanced by the withdrawal of the same from the sea by marine plants and animals, the casting up of these upon the shore, the removal of fishes by man and aquatic birds, the tearing off from the sea, and scattering upon the land, of salt water by high winds, and the deposition of shells and purely sedimentary matter at the bottom of the ocean.

§ 344. When dry or warm air passes over the surface of the sea, or when the latter is heated by the sun's rays, the water is evaporated in a pure state, the mineral constituents being left behind. As this process goes on rapidly and to an immense extent, the sea would gradually become more and more salt were it not for the fresh water returned to it by rain and rivers.

§ 345. The water which thus rises into the air by evaporation makes the air lighter, vapour of water being less dense than air. The ceaseless currents in the air (I. § 23) bear the moist air to other places having different temperatures. Warm air saturated, or nearly so, with vapour of water, must give up a part of its water when cooled. Clouds are formed of water condensed in this way. When a large quantity of water thus accumulates in the air, it may collect as drops and fall as *rain*; if it is previously frozen, it appears as *hail*; if it reaches the earth before collecting into large drops, it is called *fog* or *mist*; if it is frozen when in the state of mist, it is *snow*; if it is condensed upon the surface of the earth by the nightly cooling of the earth, it is called *dew*; and frozen dew, or dew deposited in the frozen state, is called *hoar-frost*. In all cases, water which reaches the earth from the sky holds in solution some of the gases of which the air is formed, especially, of course, those which are most soluble in water. Thus rain-water, especially that which falls at the commencement of a shower after long drought, contains appreciable quantities of ammonia and nitrous acid. It also contains carbonic acid, oxygen, and nitrogen, nearly in the proportion of their solubility. Altogether 100 vols. of rain-water contain about 2·5 vols. of gas. Rain-water collected towards the end of a heavy shower is almost absolutely pure.

§ 346. The water which falls as rain or snow (which afterwards melts) seeks, by the attraction of the earth, to attain the lowest level. It may find its way at once along the surface of the earth, as rivulets, streams, &c., to rivers; or it may first collect in marshy reservoirs, from which it subsequently issues: in either case it generally takes up the oxides of calcium, potassium, sodium, magnesium, and iron, combined with carbonic, silicic, or hydrochloric acids. But in such a case the quantities of these bodies held in solution is usually small. A more important and harmful ingredient in such waters is the vegetable and animal remains which it meets with and partly dissolves. The more rocky and broken the course of a river is, the more completely are such carboniferous and nitrogeniferous bodies oxidized by the oxygen which the water absorbs from the air, and therefore the purer and more fit for drinking is the water.

§ 347. It often happens that rain-water, especially such as falls upon the sides of hills whose summits are exposed, and whose rocky layers are so turned up as to present their edges, finds its way between the strata, and descends into the valleys beneath the soil, and even beneath one or more of the upper strata of which the rocky part of the earth is formed. It travels until it finds or makes some vent through the upper layers of the earth, and appears as a natural spring. Such water, during its passage through the earth, becomes disembarrassed by filtration of almost all its organic (animal or vegetable) impurities; but it usually dissolves in its course more or less of the rocks over which it passes. In this it is greatly aided by the carbonic acid which it has brought from the air, or which is freed from other rocks which it meets with. Water which holds carbonic acid in solution has the power of dissolving small quantities of almost all rocks, and especially carbonate of calcium. Spring-water therefore generally contains a larger quantity of mineral matter than river-water.

§ 348. The total quantity of solid matter dissolved in a water is easily ascertained by evaporating a known volume of it in a weighed dish at a gentle temperature. The presence in water of salts of calcium and magnesium imparts to the water "hardness." Water which contains these substances has a peculiar harsh feeling when rubbed between the hands, owing to the removal by these salts of the fat natural to the surface of the skin. Such waters require a large amount of soap before they form a lather. The hardness of waters, and therefore approximately the amount of calcium and magnesium salts which they contain, may accordingly be measured by determining the quantity of soap-water of a given strength which is required to form a lather or permanent froth with them.

§ 349. Waters which contain carbonate of calcium or magnesium dissolved in an excess of carbonic acid give up that carbonic acid on exposure to the air, and more quickly on boiling. Spring-water "sparkles" on this account. The sparkling is the escape of minute bubbles of carbonic acid; and the consequence of such escape is the deposition of the ordinary insoluble carbonate of calcium. Such is the process which takes place in the petrifying springs; and to this cause is due the formation of "Stalactites" and of marble. The same process takes place more rapidly on boiling; and the incrustation or fur on kettles and boilers is mainly carbonate of calcium, magnesium, and iron deposited by this means.

Many spring-waters contain a large quantity of iron as a carbonate dissolved in carbonic acid. Such waters are called chalybeate, and have the peculiar inky taste of iron salts.

The gases dissolved in spring-water are mainly oxygen and nitrogen (derived from the air), carbonic acid (derived from the carboniferous rock-sand, to a small extent from decayed organic matter), and sulphuretted hydrogen (the origin of which is often obscure, but which is generally formed when organic matter comes into contact with and reduces the metallic sulphates).

For the detection and determination of the ingredients, mineral and organic, of waters, the student is referred to special treatises.

QUESTIONS.

PART I.

1. Explain the difference between the sensations of heat and cold. What are the chief sources of heat? (§§ 1–16.)
2. State the law for the expansion of gases by heat. 80 cubic inches of air at 60° C. are heated to 95° C.; what will be the volume of the heated air? (§ 18.)
3. Describe the formation of the trade-winds. (§ 23).
4. How can it be shown that different liquids expand unequally for the same increase of temperature? Describe the variation in the density of water near its freezing-point. (§§ 28, 29, 31).
5. Describe the formation and some of the consequences of the "Gulf-stream." (§§ 33, 34.)
6. Arrange the following substances in the order of their expansibility:—copper, lead, zinc, iron, glass, platinum. What is the principle of the gridiron- and of the mercurial compensating pendulum? (§§ 36, 37.)
7. Describe Fergusson's Pyrometer. (§ 39.)
8. If a rod of iron, which is an inch long at 0° C., becomes 1·001 inch at 100° C., what will be the increase of size of a cubic inch of iron when heated from 0° C. to 100° C.? (§ 43.)
9. Describe the "differential thermometer." Describe the manufacture of a mercurial thermometer. (§§ 48, 52–54.)
10. Describe the Fahrenheit, Réaumur, and Centigrade scales. (§§ 55, 56.)

What temperature Fahrenheit corresponds to 10° Centigrade?
„ „ Centigrade „ 10° Fahrenheit?
„ „ Réaumur „ —40° Fahrenheit?
„ „ Centigrade „ 2° Réaumur?
„ „ Fahrenheit „ 0° Réaumur?
„ „ Réaumur „ 17° Centigrade?

11. Describe the self-registering maximum and minimum thermometer. (§ 58.)

12. Explain what is meant by capacity for heat (§ 65) and specific heat (§§ 69–77). A lump of sulphur weighing ½ lb., and having the temperature 10° C., is placed in a quantity of water having the weight 4 lb. and the temperature 90° C. After a time the temperature of the water and sulphur are both found to be 88° C.; what is the specific heat of the sulphur? (§§ 69–77.)

13. Describe one form of calorimeter. What gas has the greatest specific heat? How does the specific heat of a solid vary with the temperature? (§§ 78–84.)

14. Define latent heat, and show how the latent heat of vapours may be determined. (§§ 85–96.)

15. Describe the action of a freezing-mixture. (§§ 97–99.)

16. How is the tension of the vapour of a liquid affected by the temperature? (§§ 104–109.) Explain the cryophorus. (§ 117.)

17. What is the cause of rain? and why are the tops of hills subject to be covered with clouds? (§ 125.)

18. How is the boiling-point affected by pressure? Describe an apparatus by means of which the pressure exerted by steam of various temperatures may be measured. (§ 138.)

19. Distinguish between conduction, convection, and radiation of heat, giving examples of each. (§§ 141, 164, 169.) What class of bodies conduct heat the best? which is the best conductor amongst the metals? (§§ 151, 153.)

20. How is the convection of heat applied to the warming of rooms? (§§ 165–167.) How does the convection of heat influence the air (§ 23) and sea (§ 33)?

21. What class of bodies are the best reflectors of heat? What is the law of reflexion? (§ 176.)
22. What is the velocity of heat? What solid body allows most heat to pass through? (§§ 172, 184.)
23. What is the law connecting the temperature and the distance from the source of heat? (§ 175.)

PART II.

1. Describe two of the best methods of preparing oxygen; how much heavier is it than hydrogen? How do you distinguish it from nitric oxide and from protoxide of nitrogen? (§§ 76, 75, 127, 131.)
2. Describe some of the principal forms of carbon: state how each is procured. What gaseous compounds does carbon form with oxygen? Give the composition of each. (§§ 146, 147, 154, 160.)
3. Express in symbols the reaction which takes place when hydrochloric acid is heated with black oxide of manganese. Give the relative proportions by weight of the elements described by your symbols. What are the properties of the gaseous product? (§§ 180, 6, 182, 183, 184.)
4. How is ammonia obtained? What is its composition? What bulk of each of its constituent gases would be formed by a cubic inch of ammonia, supposing it completely decomposed by a series of electric sparks? (§§ 134, 136, 139, 133.)
5. What are the principal salts present in sea-water? How may you procure pure water? (§ 342.)

6. What is the common mode of preparing nitric acid? (§ 116.)
7. Describe how you would distinguish oxygen from common air. What class of bodies do we call oxides? Name some oxides of an acid nature, and some basic oxides. (§§ 111, 52, 57, 62.)
8. Describe the structure of the flame of a common candle; and explain why the flame loses its brightness when a current of common air is blown into it. (§§ 307, 308.)
9. One hundred volumes of nitrogen are given: how many volumes of oxygen must be added in order to obtain a mixture having the same composition as pure atmospheric air? (§ 330.)
10. What volume of oxygen is required for the complete combustion of one gramme of carbon? (Sixteen grammes of oxygen measure 11·2 litres.) (§ 20.)
11. Write the formulæ of hydrochloric acid, water, nitric acid, nitrous acid, carbonic oxide, sulphurous acid, sulphuric acid, hypophosphorous acid. (§§ 191, 88, 115, 122, 160, 224, 229, 264.)
12. Write the names of the substances which have the following formulæ:—H_2S, PCl_5, $POCl_3$, CH_4, N_2O, NO, HNO_3, C_2H_4, $SiFl_4$. (§§ 236, 270, 273, 169, 129, 125, 116, 164, 291.)
13. Give the tests for sulphuric acid, nitric acid, and hydrochloric acid. (§§ 235, 118, 195.)
14. If a mixture of 90 vols. of hydrogen and 20 vols. of oxygen are exploded, what will be the volume of the product? (§ 97.)
15. Show how to deduce the density of steam. (§ 38.)
16. How many equivalents of each element present are there in the body $2SO_2, 3H_2O4NO_2$?
17. Whence does a plant get its carbon? A living plant is shut up in a room containing atmospheric air; how will the plant affect the air during the day, and during the night? (§§ 332, 333.)
18. What chemical process takes place in the lungs of animals? (§ 331.)

19. Explain fully the manufacture of oil of vitriol (sulphuric acid. (§ 230.)
20. How is the pentachloride of phosphorus prepared? and what happens when it is thrown into water? (§§ 270, 271.)
21. Mention some sources of silicic acid. What is the action of hydrofluoric acid upon silicic acid? (§§ 277, 291.)
22. What is the composition of cyanogen? and how is it obtained? How is hydrocyanic acid obtained? (§§ 173, 177, 176.)
23. What are the tests for ammonia? (§ 143.)
24. A cubic litre of hydrogen weighs 0·089 gramme. What volume of hydrogen can be got by treating 70 grammes of zinc with an excess of H_2O and H_2SO_4? (The equivalent of zinc is 65·2.)
25. In 100 lb. of nitrate of potassium, how many pounds are there of O, of N, and of K (the equivalent of K being 39)?

INDEX.

PART I.

Page
Absorption 65
Absorption by gases 70
Air-thermometer 9
Calorimeters 38
Capacity for heat 33
Centigrade thermometer 28
Change of physical state (as source of heat) 5
Chemical change (as source of heat) 6
Cloud 53
Cold 1
Compensation pendula 19
Compression (as a source of heat). 5
Conduction of heat (gases) 61
  „ „ (liquids) 61
  „ „ (solids) 58
Convection of heat 63
Cryophorus 50
Diathermanous bodies 69
Differential thermometer 24
Dynamical theory of heat 3
Earth (the) a source of heat 3
Ebullition 54
Electrical discharge (a source of heat) 6
Evaporation 46
Expansion by heat (gases) 7
  „ „ (liquids) 11
  „ of solids (cubic) 21
  „ „ (linear) 17
Fahrenheit's thermometer 28
Fire-balloon 9
Freezing-mixture 45
Friction (as a source of heat) 4
Fog 53
Gulf-stream 17

Page
Hail 53
Hygrometers 53
Intensity varies with distance. 66
Latent heat 41
Liquefaction of gases 46
  „ solids 45
Maximum and minimum thermometer 31
Maximum density of water 14
Mist 55
Parabolic reflectors 68
Pyrometer (Fergusson's) 20
Pyrometers 24
Quantity of heat 33
Radiation of heat 64
Rain 53
Rate of heat 65
Réaumur's thermometer 28
Reflexion 65
Registering thermometer 31
Sensation of heat and cold 2
Snow 53
Sources of heat 3
Specific heat 36
Specific heats (Table of) 40
Sun (the) 3
Temperature 32
Temperatures (natural) 30
Tension of vapours 47
Thermometer (mercurial) 25
Thermometers 22
Trade-winds 10
Transmission of heat 65
Unequal expansion of crystals 21
Ventilation 10
Volatilization 46

PART II.

Page
Acids ... 93
Affinity (chemical) ... 80
Ammonia ... 123
Ammonium-amalgam ... 127
Animals (relation of, to the air) ... 195
Atmosphere (the) ... 194
Atomic hypothesis ... 78
„ weight ... 79, 82
Bases ... 93
Bat's wing burner ... 188
Binoxide of hydrogen ... 113
Bisulphide of carbon ... 166
Bleaching-powder ... 142
Blowpipe ... 189
Brimstone ... 158
Bromic acid ... 148
Bromides of phosphorus ... 177
Bromide of silicon ... 181
Bromine ... 147
Bunsen's burner ... 188
Calculation (numerical) ... 103
Carbon ... 128
Carbonic acid ... 130
Carbonic oxide ... 133
Catalysis ... 110
Charcoal ... 192
Chemical union and mechanical mixture ... 74
Chloric acid ... 143
Chloride of bromine ... 149
Chloride of nitrogen ... 147
Chlorides of phosphorus ... 175
Chloride of silicon ... 180
Chlorides of sulphur ... 167
Chlorine ... 140
Chlorohydrocarbons ... 146
Chokedamp ... 137
Coal ... 192
Coke ... 193
Combination by volume ... 83
Combining proportions ... 81
Combustion ... 182
Comparison between chlorine, bromine, and iodine ... 154
Cyanogen ... 138
Davy's lamp ... 191
Decay ... 123

Page
Diamond ... 128
Disinfecting powder ... 142
Elements ... 71
„ (Table of) ... 72
Empirical formulæ ... 89
Ethylen ... 134
Eudiometer ... 197
Ferrocyanide of potassium ... 138
Firedamp ... 137
Flame ... 182
Flowers of sulphur ... 158
Fluoride of silicon ... 181
Fluorine ... 155
Fuel ... 191
Galena ... 157
Graphite ... 128
Gunpowder ... 168
Hardness (of water) ... 201
Heavy carburetted hydrogen ... 134
Hydride of silicon ... 180
Hydriodic acid ... 153
Hydrobromic acid ... 148
Hydrochloric acid ... 144
Hydrocyanic acid ... 139
Hydrofluoric acid ... 155
Hydrogen ... 105
Hydrosulphuric acid ... 164
Hypochlorous acid ... 143
Hypophosphorous acid ... 173
Iodic acid ... 151
Iodide of nitrogen ... 153
Iodides of phosphorus ... 177
Iodine ... 150
Lampblack ... 128
Light carburetted hydrogen ... 136
Light of flame ... 187
Lucifer-matches ... 170
Marsh-gas ... 136
Metaphosphoric acid ... 172
Multiple proportions ... 77
Muriatic acid ... 144
Nitric acid ... 116
„ (anhydrous) ... 118
Nitric oxide ... 120
Nitride of phosphorus ... 175
„ silicon ... 180
Nitrogen ... 114
Nitrous acid ... 119

Page
Nitrous oxide 121
Nomenclature 90
Oil of vitriol........ 161
Olefiant gas 134
Oxide of chlorine........ 143
Oxides of nitrogen 115
Oxychloride of phosphorus........ 176
Oxygen 98
Oxyhydrogen blowpipe 110
Ozone 102
Paracyanogen 139
Pentachloride of phosphorus ... 176
Perchloric acid........ 152
Periodic acid 144
Peroxide of nitrogen 118
Petroleum........ 193
Phosphoretted hydrogen........ 173
Phosphoric acid 171
,, ,, (anhydrous) ... 171
Phosphorous acid (anhydrous). 172
,, ,, (hydrated)... 173
Phosphorus 169
,, (amorphous) 170
Plants (relation of, to the air).. 195
Plumbago........ 128
Prussic acid 139
Pyrites 157
Pyrophosphoric acid 172

Page
Rain-water 200
Rational formulæ........ 89
River-water 200
Safety-lamp 191
Salts 93
Sea-water 199
Silica........ 179
Silicic acid 179
Silicon 177
Spirit of salt........ 145
Spring-water........ 201
Sulphide of hydrogen 164
,, nitrogen 167
Sulphides of chlorine 167
Sulphides of phosphorus........ 177
Sulphur........ 157
Sulphuretted hydrogen 164
Sulphuric acid........ 161
,, (anhydrous) ... 160
Sulphurous acid 159
Sulphydric acid 164
Symbols 88
Synthesis 75
Terchloride of phosphorus 175
Water 109
Waters (natural)........ 199
Wood 191
Zincblende 157

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